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Contributions to Environmental Specimen Banking

Editors: M. Stoeppler and H. W. Dürbeck

2. Decomposition and Stability Studies of Methylmercury in Water

by

Riaz Ahmed
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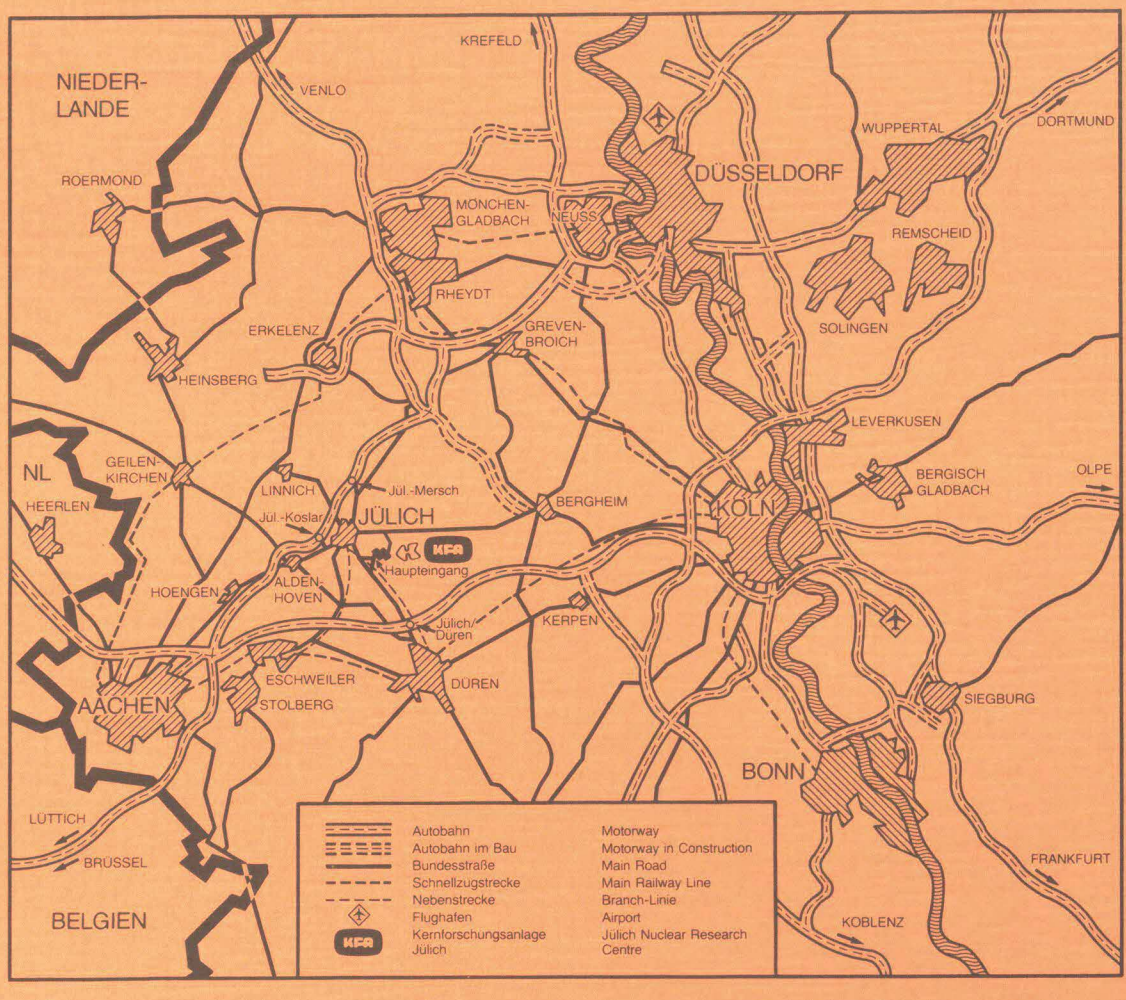

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2. Decomposition and Stability Studies of Methylmercury in Water

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Editorial Preface

This series of "Jül-Spec" reports is intended to the presentation of detailed and extensive informations in the field of Environmental Specimen Banking (ESB). Primarily, the reports will be in close relation to the research program of the "Institute of Applied Physical Chemistry" within the frame of the current ESB-program in the Federal Republic of Germany. Therefore, a substantial part will be dedicated to results and discussions of these activities covering the strategies and techniques for collection, preparation and long-term storage of numerous environmental specimens. Moreover various modes of physical, physicochemical and chemical methods for the characterization of research and reference materials will be presented including investigations for a better understanding of transportation and degradation processes determining the fate of inorganic, organometallic and organic compounds. Finally, contributions addressing the scientific and logistic basis of the entire ESB-program will be integrated, particularly dealing with ecological, biological, geochemical and monitoring aspects in order to provide additional and important background informations.

Jül-Spec-330 (1985) "Studies for Homogenization of samples at low temperatures with regard to the parameters required for the Environmental Specimen Bank" may be regarded as the first contribution, other technical and more general contributions either written in German or English are in preparation and will appear in the near future.

Juelich, March 1986

Markus Stoeppler and Hans Werner Dürbeck

Zersetzungs- und Stabilitätsstudien für Methylquecksilber in Wasser

Zusammenfassung

Es wurde die Langzeitstabilität von Hg^{+2} und Methylquecksilberchlorid (MeHgCl) sowie der Abbau von MeHgCl unter verschiedenen Bedingungen untersucht.

Die Untersuchungen wurden mit starken Säuren (HCl, HNO_3, H_2SO_4, $HClO_4$) und Natriumhydroxid mit und ohne Zusatz bestimmter Reagentien (NaCl, H_2O_2, L-Cystein) bei Raum- und erhöhten Temperaturen, in der Dunkelheit und bei Licht (UV) durchgeführt. Für die Stabilitätsstudien wurden Gefäßmaterialien aus Borosilikatglas, Polyethylen und PTFE herangezogen. Als Nachweismethoden wurden Kaltdampf-AAS nach Anreicherung an Golddraht (Hg, überwiegend), aber auch Gas-Chromatographie mit Elektroneneinfangdetektoren (MeHgCl) sowie γ-Spektrometrie, zur Aufklärung von Abbau und Reaktionsmechanismen mit Hilfe von ^{203}Hg, herangezogen.

Die im Detail vorgestellten Ergebnisse zeigen, daß unter Lichtausschluß bis zu Säuregehalten von 25 % kaum ein Abbau von MeHgCl in Hg^{+2} stattfindet. Unter UV-Bestrahlung erfolgt jedoch abhängig von deren Intensität ein rascher Abbau des MeHgCl zu Hg^{+2}. In Gegenwart von SH-Gruppen (L-Cystein) wurde eine teilweise Stabilisierung und Maskierung von Quecksilber beobachtet. Für die Langzeitlagerung wäßriger Lösungen von Hg^{+2} und MeHgCl ist neben dem Zusatz geeigneter Reagentien vor allem das Gefäßmaterial wichtig. Am günstigsten sind Glas und Quarz, weil sie sowohl Verluste als auch Kontamination verhindern.

Decomposition and Stability Studies of Methylmercury in Water

Summary

Long-term stability of Hg^{+2} and MeHgCl, and decomposition of MeHgCl under different conditions are investigated. Studies were done with acids (HCl, HNO_3, H_2SO_4, $HClO_4$) and sodium hydroxide with and without adding different reagents (NaCl, H_2O_2, L-Cystein) at room and higher temperatures with and without UV-light. For the stability studies container materials used were of Borosilicate glass, polyethylene and PTFE. Measurements were done using mostly cold vapour AAS after preconcentration on gold wool, but also Gas-Liquid-Chromatography with Electron capture detector and γ-spectrometry were used to understand the decomposition and reaction mechanisms by labelling with ^{203}Hg. The given detailed results show that in the absence of light MeHgCl does not decompose to Hg^{+2} even in the presence of 25 % acids. MeHgCl is also not easily decomposed by heating in the presence of low acid concentrations. But with UV-light decomposition of MeHgCl to Hg^{+2} takes place immediately depending upon the intensity of UV-light. In the presence of SH-groups (L-cystein) partial stability and complexation of mercury was observed. For long term storage of Hg and MeHgCl at low concentrations, in addition to certain reagents, the material of the container is also important. Glass and quartz containers are better as they minimize losses and contamination.

2. CONTENTS

3. INTRODUCTION

Mercury and organomercury compounds particularly methylmercury are well known for their toxic properties and thus are important environmental pollutants (1). Much work has been done for the analysis of mercury and methylmercury (2,3). Most hitherto published papers on the analysis of methylmercury are about the analysis of methylmercury in fish samples (3), because the mercury present in fish is predominantly methylmercury (4,5). Fish in water can accumulate methylmercury several orders of magnitude more than the concentration of mercury or methylmercury in water. Studies have been done about the decomposition of methylmercury in fish samples using higher concentrations of acids (6,7). With the availability of new and more sensitive analytical techniques, the interest for the analysis of mercury and methylmercury in water has increased (8,9). For the decomposition and measurement of methylmercury in aqueous samples one cannot use as high concentrations of acids as for fish samples due to the extremely low concentrations of mercury in water. Consequently large volumes of water are required for analysis. Therefore a need was felt to do decomposition studies of methylmercury in water using acid concentrations which can practically be used for water analysis.

It has been reported that atomic mercury can be taken up into the cystein disulfide bridges of proteins (10). It has also been reported that sulfhydryl compounds (L-cystein) act as an effective photosensitizer for photochemical methylation of inorganic mercury (11). There is a possibility of mercury entering the biosphere as a Hg-cystein complex (12). Keeping in view the above points and considering the possibility of the presence of sulfhydryl compounds in environmental compartments particularly sea water and rain water etc.; it looked appropriate to investigate the behaviour of methlymercury regarding its decomposition in the presence of cystein which is a typical sulfhydryl compound.

Much work has been published about the stability of ionic mercury in solutions (13-17). Very little is known, however, about the stability of methylmercury in aqueous systems (18-20). Hardly there is any reference available about the stability of methylmercury in aqueous systems close to natural levels of mercury and methylmercury. Therefore in this study long term stability has been investigated for methylmercury in the presence of different reagents. This also included stability studies in containers of different types of materials.

3.1 Aim and Framework of the Investigation

Methylmercury is much more toxic than ionic mercury and is mostly found in food (fishes etc.) thus is of particular significance in environmental pollution.

There is much controversy about the methylation and demethylation of mercury in different compartments of the environment (21). Causes for the presence of high amounts of methylmercury in fishes are still not completely known. Although the mercury source for fishes is sea water, but sea water contains only spurious amounts of methylmercury. Actually the behaviour of MM in aqueous systems at low levels is still not sufficiently elucidated. In this work relatively low levels of MM were used (range 0.005 to 1.0 µg/l MM) and this investigation was done to see:

1. The behaviour of MM in water, when exposed to light, heat and in the presence of different reagents.
2. The effect of sulfhydryl compounds (L-cystein) on the decomposition, stability and measurement of MM in water.
3. Decomposition studies of MM in water by heating with acids under low pressures.
4. Long-term stability studies of MM at low levels in aqueous systems in different types of container materials.

4. EXPERIMENTAL

CHEMICALS: All the acids used i.e., HCl, HNO_3, $HClO_4$, H_2SO_4 were of suprapur grade from E. Merck, BRD. NaCl, L-cystein, $SnCl_2$ + H_2SO_4, methylmercury, HgO, H_2O_2, Na_2SO_4, NaOH, Sodium acetate, Toluene were of p.a. grade from E. Merck. Labelled methylmercury (1mCi = 37 x 10^6 Bq) was from Amersham, U.K.

APPARATUS: Pyrex glass flasks, quartz glass flasks, cylinders, beakers, pipettes, digestion vessels of quartz glass, micro-pipettes, N_2 gas cylinders etc.; UV-lamp for decomposition studies was of 150 W.

An Atomic Absorption Spectrometer, Model 400, manufacturer Bodenseewerk Perkin-Elmer, BRD, with a mercury vapour lamp at 0.2 A/15 V as a light source, wave-length = 253.7 nm, slit width = 2.0 nm was used. The mercury reduction vessel was of pyrex glass with a volume of 1 litre. Additional equipment was a Recorder SE 120, Goertz Metrawatt, BRD. The automatic heating and gas-flow control system used was of own design, constructed by the workshop of Dr. Beerwald, Bochum BRD.

A gas-liquid chromatograph, Model 5710 equipped with an electron capture detector, manufacturer Hewlett Packard U.S.A., was used for the measurement of methylmercury. Other conditions were adjusted as given under (5,22).

column : 20 % carbowax with gas chrom Q 80 - 100 mesh, with i.D. = 3 mm, length = 1.5 meter, gas flow rate 60 ml/min

Injection Temp. = 200 ^{o}C

Column. Temp. = 160 ^{o}C

Detector Temp. = 300 ^{o}C

Retention time for MM 4.0 minutes.

Multichannel Analyzer Series 80 of Canberra U.S.A. with software Canberra Spectron F Version V2 D1 computer PDP 11/03 with 64 K Memory was used. Other parameters selected were

^{203}Hg = 279 KeV

HWZ = 46.6 d

Ge(Li)-detector	143 cm^3
Resolution	2.0 keV
Efficiency	25.5 % at 1.33 MeV (Co-60)
Counting time	500 seconds.

CVAAS-PROCEDURE: 50 ml of (10 % $SnCl_2$ + 20 % H_2SO_4) solution was taken in the reduction vessel. A known volume of the sample usually from 0.001 to 1.0 ng/ml Hg was added. N_2 gas was passed through this solution at a rate of 2.0 to 2.5 l/minute for one minute and mercury vapours are taken away by N_2, which is at first passed through 25 % NaOH solution and then distilled water to absorb acid vapours and other soluble impurities and then mercury vapours are deposited on gold wool kept in a quartz glas tube. Then the flow of N_2 through the reduction vessel is stopped and is passed through gold wool only at a rate of 50 - 100 ml per minute. At the same time the gold wool is heated to 700 - 800 ^{o}C. Mercury vapours deposited on the gold wool are evaporated and allowed to travel through the quartz glass cuvette where the concentration of mercury as vapours is measured. After the measurement of the sample a known amount of standard solution is added to the same solution and measured. The gold wool is heated for 10 seconds and in order to increase the rate of determinations it is cooled with pressurized air so that the system is ready for the next measurement. Apparatus and procedure have been mentioned already (23) and will be described together with all recent modifications in detail elsewhere (24).

5. RESULTS AND DISCUSSIONS

5.1 Precision and linearity of the applied method

The CVAAS method of cold vapour Atomic Absorption Spectrophotometry developed in this laboratory has a detection limit $\leqslant$0.1 ng/l for (100 ml) water samples. The relative standard deviation for the analysis of mercury at 1 ng levels (absolute) is $<$5 %. It has a wide linearity range i.e., from 0.1 ng to 10 ng mercury concentrations (fig-1). Mercury concentrations used for the experiments were from 0.005 to 1.0 /ug/l of Hg. In this method the solution used for the reduction of ionic Hg to atomic Hg was 10 % $SnCl_2$ + 20 % H_2SO_4 and it was found that this solution did not decompose methylmercury (MM) under the used experimental conditions.

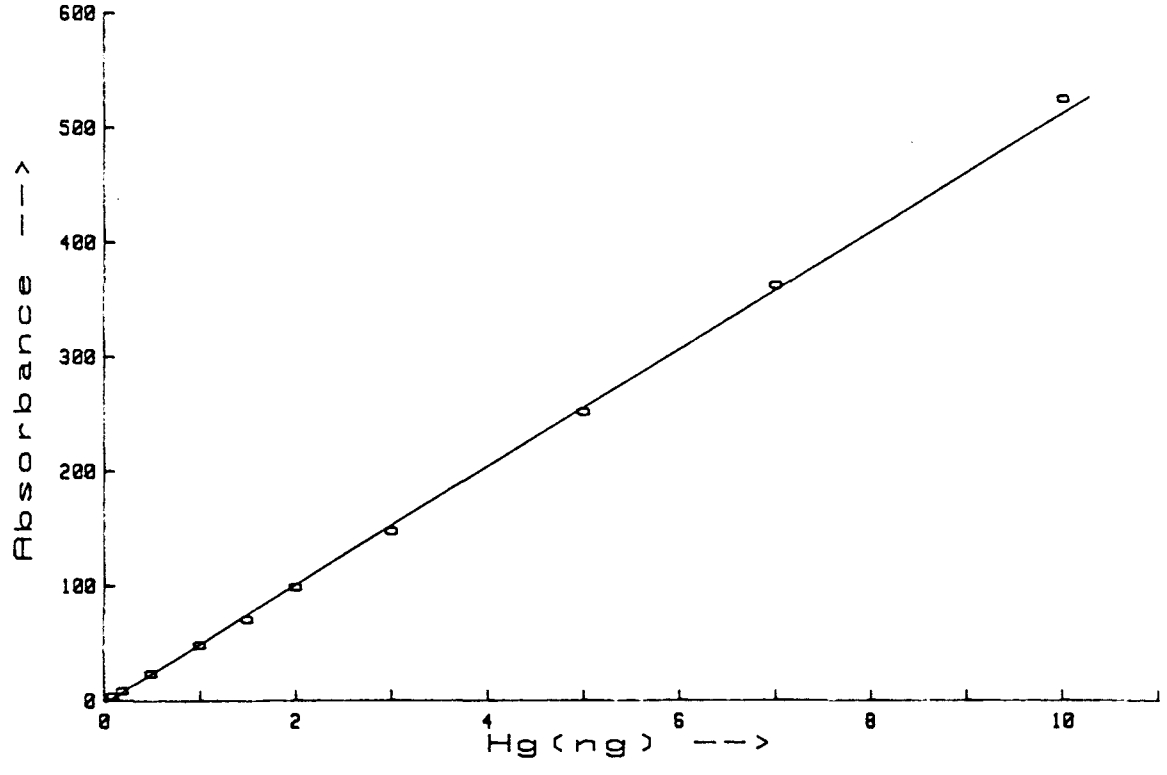

Fig. 1: Linearity curve for the analysis of Hg by CVAAS

5.2 Decomposition of MM in the presence of different reagents and effects of UV-irradiation

5.2.1 Stability of MM during storage and measurement of ionic Hg by CVAAS

To investigate the possibility of analysis of ionic mercury in the presence of methylmercury three solution were prepared containing ionic mercury, ionic Hg + MM (Methylmercury) and ionic mercury + MM + 0.05 % cystein in pyrex glass flasks covered with Al-foil and measured over a period of ten days. It was found that methlymercury was quite stable in solutions and did not decompose at all during the reduction step for the analysis of ionic mercury (Table-1).

Table. 1: Analysis of ionic Hg by CVAAS in the presence of Methylmercury (MM)

		Hg(ng/ml) After (days)				
Sample	Reagents Added.	0.0 d	3.0 d	4.0 d	7.0 d	10.0 d
0(2)	5 % HCl + 0.38 ng/ml Hg	0.36	0.36	0.36	0.36	0.34
5(2)	5 % HCl + 0.38 ng/ml Hg + 0.70 ng/ml MM	0.36	0.36	0.36	0.41	0.38
6(2)	5 % HCl + 0.05 % cystein + 0.38 ng/ml Hg + 0.70 ng/ml MM	0.39	0.40	0.40	0.40	0.37

Samples were prepared in pyrex glass flasks covered with Al-foil

5.2.2 Decomposition of MM in the presence of NaCl + HCl in pyrex glass flasks covered with Al-foil

Reagents like NaCl and HCl have been and are being extensively used and are added to different environmental samples for extraction of methylmercury by organic compounds (Toluene, benzene) and subsequent analysis of MM by Gas Chromatography. Decomposition studies of MM in the presence of these reagents in pyrex glass flasks covered with Al-foil were done (fig-2). Higher concentrations of HCl or of NaCl alone do not decompose MM so quickly, but when 15 % NaCl + 2.2 M HCl is added, it decomposes MM up to 40 % within one day and this very combination has been extensively used for extraction/separation of MM (25). It can be seen from fig. 2 that in the presence of

these reagents losses of MM may take place if more time is spent for extraction purposes.

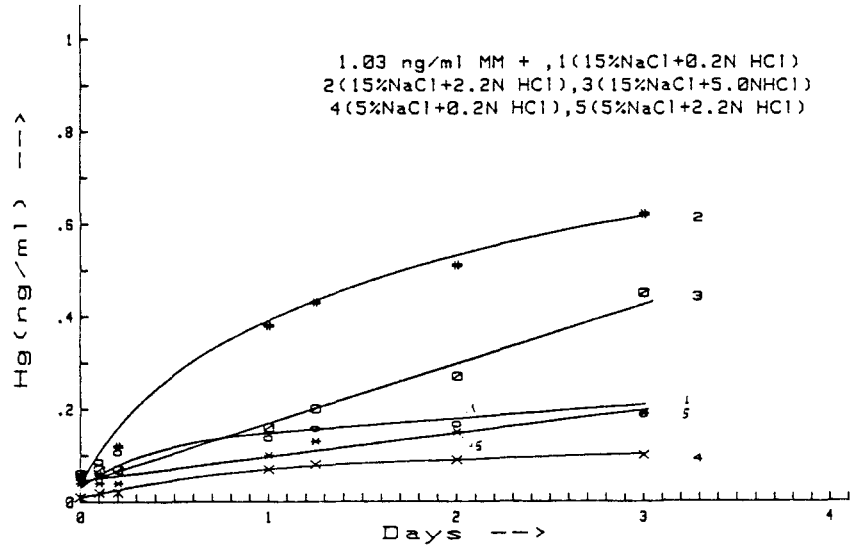

Fig. 2: Decomposition of MM in pyrex glass flasks covered with Al-foil.

5.2.3 Decomposition of MM in the presence of NaCl + HCl and light in quartz glass flasks

Decomposition studies of MM in the presence of NaCl and HCl in quartz glass flasks kept as such in the laboratory were also done. It can be seen from fig-3 that decomposition of MM is very rapid and in the presence of 15 % NaCl + 2.2 N HCl, completely the MM decomposes in less than 4 hours. This rapid decomposition of MM is only due to UV-light which passes through quartz glass very easily and at day time comes into the laboratory through diffused sun light.

To study the effect of UV-light on the decomposition of MM in the presence of NaCl and HCl different solutions were prepared in quartz glass flasks and exposed to UV-light (Table-2). As can be seen from Table-2, MM decomposes completely in less than 20 minutes in the presence of UV-light.

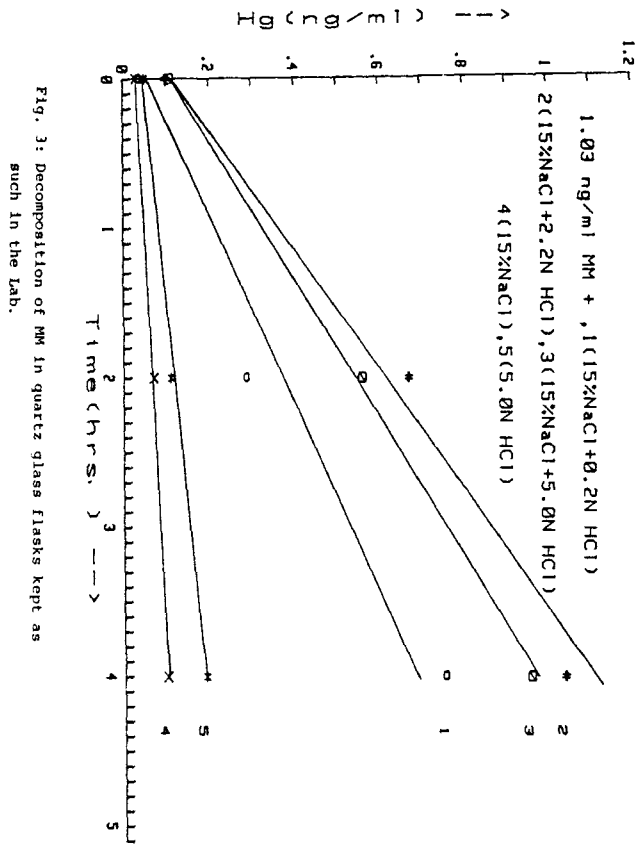

Fig. 3: Decomposition of MM in quartz glass flasks kept as such in the Lab.

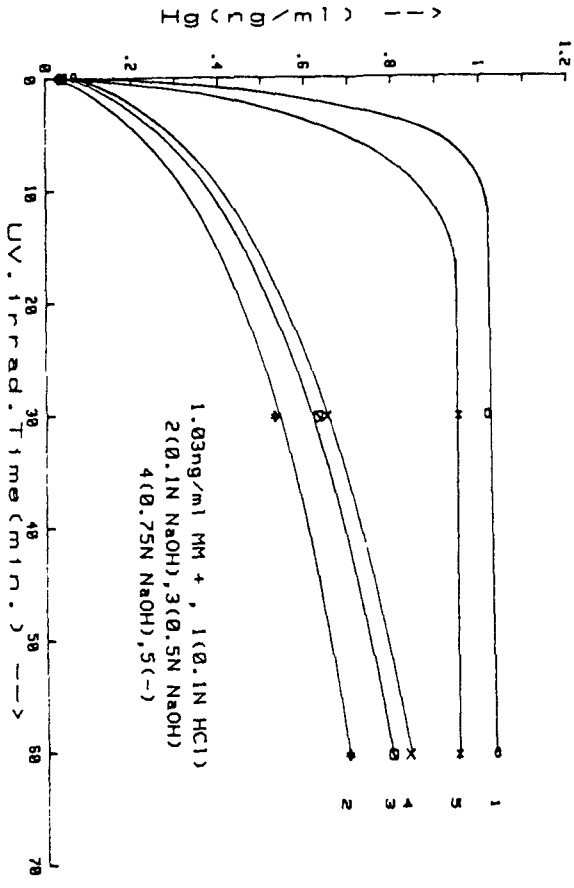

Fig. 4: Stability and losses of MM in the presence of NaOH and UV-light.

Table 2: Decomposition of MM in the presence of HCl, NaCl with UV-light

Sample	Reagents Added	Hg-added as MM(ng/ml)	Hg measured (ng/ml) Without UV	20 min UV
1	15.0 % NaCl	1.03	0.003	1.03
2	50.0 % HCl	1.03	0.006	1.04
3	15.0 % NaCl + 1 % HCl	1.03	0.016	1.05
4	15.0 % NaCl + 5 % HCl	1.03	0.013	1.06
5	15.0 % NaCl + 10 % HCl	1.03	0.045	1.08
6	15.0 % NaCl + 20 % HCl	1.03	0.016	1.03
7	15.0 % NaCl + 30 % HCl	1.03	0.016	1.09
8	15.0 % NaCl + 50 % HCl	1.03	0.013	1.06

5.2.4 Decomposition of MM in the presence of NaOH and UV-light

Solutions with different concentrations of NaOH were prepared and exposed to UV-light (fig-4). MM is not so quickly decomposed with UV in the presence of NaOH as in the presence of HCl or NaCl. Decomposition of MM is less at lower concentrations of NaOH.

Table 3: Decomposition studies of MM in the presence of different acids without and with UV

Sample No.	Reagents added	Hg (ng/ml) measured without UV after 0.0 days	1.0 days	2.0 days	3.0 days	4.0 days	Hg(ng/ml) with UV	MM(ng/ml) added
1	10.0 % conc. HCl + 2.5 % conc. HNO_3	0.02	0.02	-	0.05	-	1.04	1.03
2	20.0 % conc. HCl + 5.0 % conc. HNO_3	0.03	0.03	-	0.05	-	1.02	1.03
3	5.0 % conc. HCl +20.0 % conc. HNO_3	0.03	0.03	-	0.05	-	0.74	1.03
4	2.0 % conc. $HClO_4$+10.0 % conc. HNO_3	0.02	0.01	-	0.02	-	0.61	1.03
5	4.0 % conc. $HClO_4$+20.0 % conc. HNO_3	0.02	0.01	-	0.02	-	0.58	1.03
6	-	0.04	0.08	0.09	-	-	1.01	1.03
7	1.0 % conc. H_2SO_4	0.04	0.07	0.09	-	-	0.98	1.03
8	2.0 % conc. H_2SO_4	0.04	0.07	0.09	-	-	0.99	1.03
9	3.0 % conc. H_2SO_4	0.04	0.09	0.12	-	-	1.01	1.03
10	5.0 % conc. H_2SO_4	0.04	0.11	0.14	-	-	1.01	1.03
11	1.0 % conc. $HClO_4$	0.06	0.08	0.09	-	-	1.02	1.03
12	2.0 % conc. $HClO_4$	0.10	0.11	0.13	-	-	1.08	1.03
13	5.0 % conc. $HClO_4$	0.06	0.06	0.08	-	-	1.02	1.03
14	10.0 % conc. $HClO_4$	0.06	0.06	0.08	-	-	1.03	1.03
15	15.0 % NaCl	0.003	-	-	-	-	1.03	1.03
16	50.0 % conc. HCl	0.006	-	-	-	-	1.04	1.03
17	15.0 % NaCl + 1 % con. HCl	0.016	-	-	-	-	1.05	1.03
18	1.0 % conc. HNO_3	0.05	0.05	-	-	0.04	1.00	1.03
19	2.0 % conc. HNO_3	0.05	0.04	-	-	0.04	0.94	1.03
20	5.0 % conc. HNO_3	0.05	0.05	-	-	0.04	0.75	1.03
21	10.0 % conc. HNO_3	0.05	0.05	-	-	0.04	0.57	1.03
22	20.0 % conc. HNO_3	0.05	0.05	-	-	0.04	0.48	1.03

5.2.5 Stability and Decomposition of MM in the presence of different acids and UV-light

Experiments were done for the decomposition of MM in the presence of different acids and of combinations of acids (table-3) which are frequently used in different ways for trace analysis of mercury in environmental samples. It was found that 1 to 5 % H_2SO_4 alone did not decompose MM for 2 days, but decomposed MM immediately when exposed to UV-light. 1 to 10 % $HClO_4$ did not decompose MM for 2 days, but decomposed MM immediately when exposed to UV-light. 10 % HCl + 2.5 % HNO_3, 20 % HCl + 5.0 % HNO_3, 5 % HCl + 20 % HNO_3, 2 % $HClO_4$ + 10 % HNO_3, 4 % $HClO_4$ + 20 % HNO_3 did not decompose MM for three days without UV. In the presence of 1 to 20 % HNO_3 no decomposition of MM takes place up to 4 days, but decomposition appears in the presence of UV-light. Complete decomposition of MM takes place in the presence of UV light only up to 2 % HNO_3 concentration. In the presence of higher concentrations of HNO_3, MM does not decompose completely even in the presence of UV-light.

5.2.6 Stability and decomposition of MM in the presence of HNO_3 and UV

Commonly HNO_3 is added to aqueous environmental samples particularly sea water for the stability of ionic Hg. Experiments were done for stability of MM in the presence of 3 % NaCl and 1 to 20 % HNO_3. NaCl was added taking into consideration that many environmental samples contain NaCl. As can be seen from table-4 MM is quite stable in the presence of NaCl and up to

Table 4: Stability of MM in the presence of NaCl + HNO_3

Days	1	2	3	4	5	6
0.0	0.10	0.10	0.10	0.10	0.10	0.10
0.25	0.06	0.05	0.06	0.06	0.07	0.04
1.00	0.06	0.06	0.05	0.06	0.06	0.05
4.00	0.09	0.08	0.07	0.07	0.08	0.08
21.00	0.08	0.08	0.07	0.08	0.10	0.04
40.00	0.10	0.09	0.09	0.10	0.15	0.03

1 = 3.0 % NaCl + 1.0 % HNO_3 + 1.03 ng/ml MM
2 = 3.0 % NaCl + 2.0 % HNO_3 + 1.03 ng/ml MM
3 = 3.0 % NaCl + 5.0 % HNO_3 + 1.03 ng/ml MM
4 = 3.0 % NaCl +10.0 % HNO_3 + 1.03 ng/ml MM
5 = 3.0 % NaCl +20.0 % HNO_3 + 1.03 ng/ml MM
6 = 3.0 % NaCl + + 1.03 ng/ml MM

20 % of HNO_3 up to 40 days. For decomposition studies of MM in the presence of higher concentrations of HNO_3, samples were exposed to UV-light for longer periods see figs. 5-6.

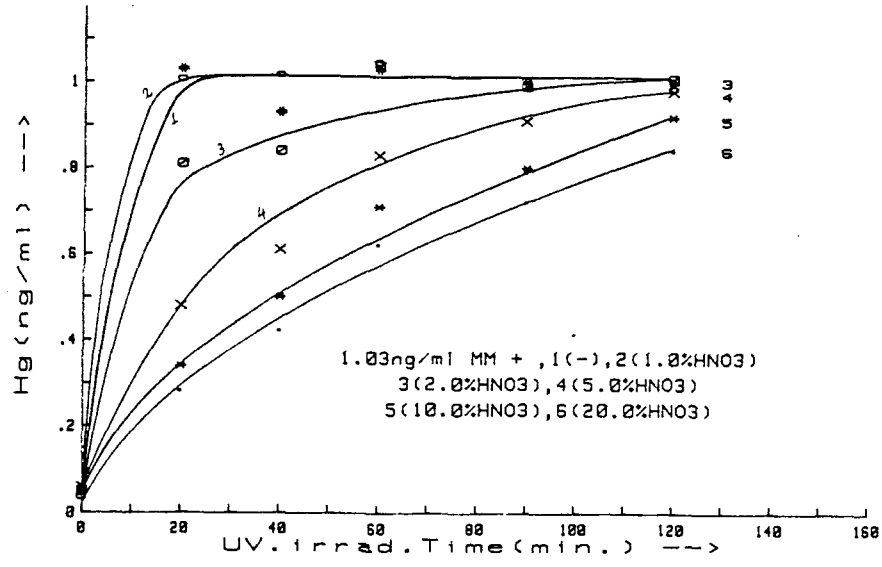

Fig. 5: Decomposition studies of MM in the presence of HNO_3 and UV-light.

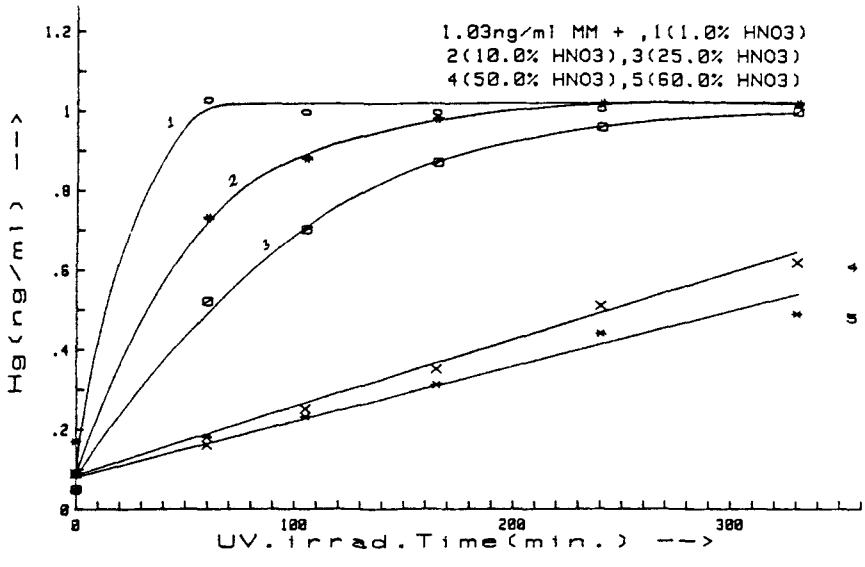

Fig. 6: Decomposition studies of MM in the presence of HNO_3 and UV-irradiation.

Decomposition of MM decreases with increase in HNO_3 concentration and it is very difficult to decompose MM when the HNO_3 concentration is more than 25 %. In the presence of NaCl and HNO_3 the rate of decomposition increases as compared to HNO_3 alone (fig.6). For example for one hour UV-irradiation only 50 % MM is decomposed in the presence of 20 % HNO_3 alone, but when 5 % NaCl is added more than 90 % of MM is decomposed (fig.7). Addition of NaCl to HNO_3 is

more effective for the decomposition of MM with UV. After 20 minute UV-irradiation nearly 55 % MM is decomposed in the presence of 10 % HNO_3 + 2.5 % HCl and nearly 85 % MM is decomposed in the presence of 10 % HNO_3 + 5.0 % NaCl (fig. 7).

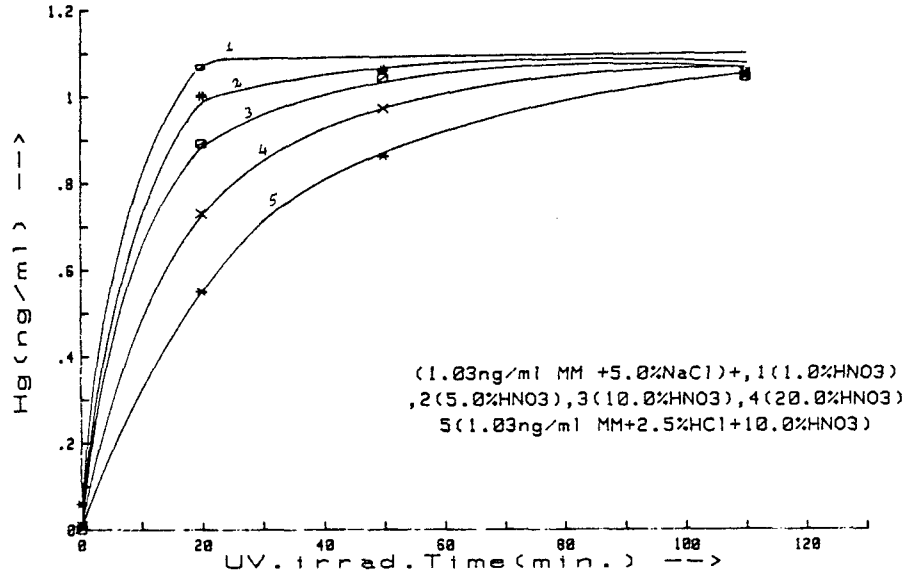

Fig. 7: Effect of chlorides on the decomposition studies of MM in the presence of HNO_3 and UV-light.

5.2.7 Decomposition of MM in the presence of acids and H_2O_2

Decomposition experiments of MM in the presence of different acids and H_2O_2 were also done. In the presence of 1 % H_2O_2 and different concentrations of acids i.e., 0.25 M to 2.0 M of HCl, HNO_3, H_2SO_4 and $HClO_4$ the percentage of MM decomposed remains the same (fig. 8). Increasing acid concentration does not increase the decomposition of MM. Nearly 17 % of MM is decomposed in the presence of 1.0 % H_2O_2 and different concentrations of HCl, 70 % of MM is decomposed in the presence of 1.0 % H_2O_2 and different concentrations of HNO_3, 55 % of MM is decomposed in the presence of 1.0 % H_2O_2 and different concentrations of H_2SO_4, 51 % of MM is decomposed in the presence of 1.0 % H_2O_2 and different concentrations of $HClO_4$. For the decomposition of MM in the presence of H_2O_2 the rate of decomposition increases with the acids $HNO_3 > H_2SO_4 \geqslant HClO_4 > HCl$.

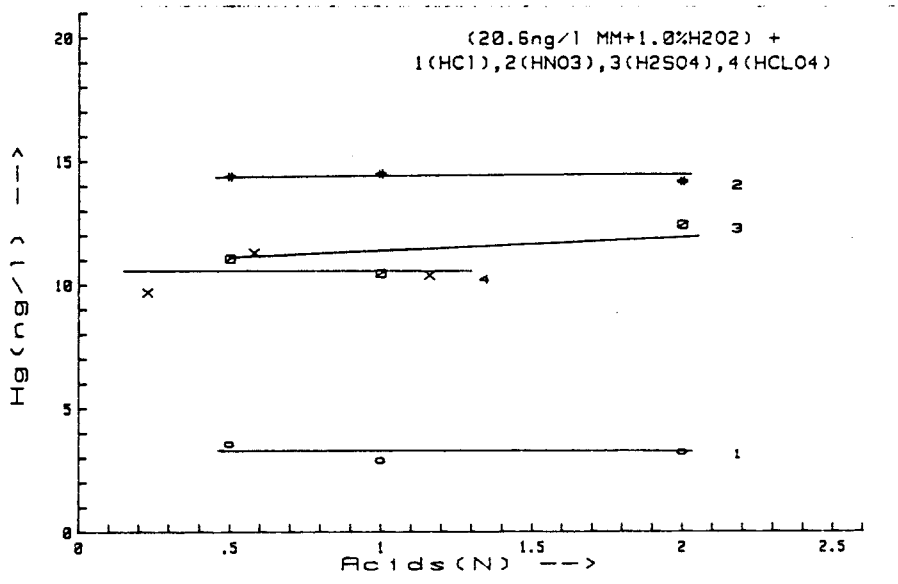

Fig. 8: Decomposition studies of MM in the presence of H_2O_2 and different concentrations of acids.

But when the acid concentration is kept constant and H_2O_2 concentration is increased, then the decomposition of MM increases with the increase in H_2O_2 concentration (fig. 9). The rates of increase in MM decomposition in the presence of HCl and H_2SO_4 are comparable and rates of increase in MM decomposition in the presence of HNO_3 and $HClO_4$ are similar (fig. 9).

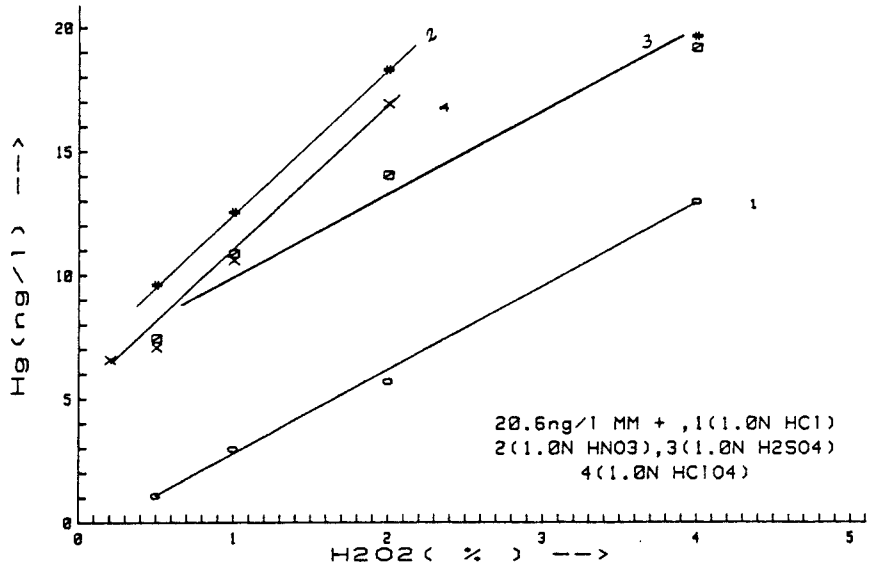

Fig. 9: Decomposition studies of MM in the presence of acids and different concentrations of H_2O_2.

Table 5: Decomposition studies of MM in the presence of acids and H_2O_2

Measured after	MM(ng/l) added.	Hg(ng/l) measured after treatment with 0.5N HCl+ 1.0% H_2O_2	1.0N HCl+ 1.0% H_2O_2	2.0N HCl+ 1.0% H_2O_2	1.0N HCl+ 0.5% H_2O_2	1.0N HCl+ 1.0% H_2O_2	1.0N HCl+ 2.0% H_2O_2	1.0N HCl+ 4.0% H_2O_2
0.0 days	20.6	4.98	3.27	2.47	1.35	3.35	12.18	14.98
1.0 days	20.6	3.61	2.95	3.28	1.14	3.02	5.75	13.00
3.0 days	20.6	3.76	2.76	5.37	1.48	3.10	5.45	12.10
UV-irrad.	20.6	21.76	20.72	20.83	20.63	21.79	22.09	29.29
		0.5N HNO_3 1.0% H_2O_2	1.0N HNO_3 1.0% H_2O_2	2.0N HNO_3 1.0% H_2O_2	1.0N HNO_3 0.5% H_2O_2	1.0N HNO_3 1.0% H_2O_2	1.0N HNO_3 2.0% H_2O_2	1.0N HNO_3 4.0% H_2O_2
0.0 days	20.6	12.94	14.35	11.95	9.61	12.53	18.27	19.62
1.0 days	20.6	13.10	14.64	15.44	10.82	13.16	18.62	19.23
3.0 days	20.6	14.39	14.49	14.20	10.08	13.61	16.44	19.13
UV-irrad.	20.6	24.47	29.10	27.98	22.94	28.24	36.19	41.59
		0.5N H_2SO_4 1.0% H_2O_2	1.0N H_2SO_4 1.0% H_2O_2	2.0N H_2SO_4 1.0% H_2O_2	1.0N H_2SO_4 0.5% H_2O_2	1.0N H_2SO_4 1.0% H_2O_2	1.0N H_2SO_4 2.0% H_2O_2	1.0N H_2SO_4 4.0% H_2O_2
0.0 days	20.6	11.06	10.46	12.44	6.17	10.80	15.51	26.65
1.0 days	20.6	12.31	13.38	13.50	7.82	13.72	23.61	43.79
3.0 days	20.6	12.16	11.14	10.27	7.45	10.86	14.02	19.16
		0.23NHClO$_4$ 1.0% H_2O_2	0.58NHClO$_4$ 1.0% H_2O_2	1.16NHClO$_4$ 1.0% H_2O_2	1.16NHClO$_4$ 0.2% H_2O_2	1.16NHClO$_4$ 0.5% H_2O_2	1.16NHClO$_4$ 1.0% H_2O_2	1.16NHClO$_4$ 2.0% H_2O_2
0.0 days	20.6	9.68	11.29	10.38	6.58	7.07	10.59	16.90
1.0 days	20.6	7.31	10.97	8.83	6.18	6.35	9.45	15.21
2.0 days	20.6	7.28	8.34	9.44	6.36	7.10	11.05	16.40
UV-irrad.	20.6	25.29	27.46	28.85	23.48	25.20	33.85	35.86

Decomposition of MM in the presence of acids and H_2O_2 takes place immediately and does not increase for longer reaction times (Table-5). As can be seen from Table-5 no increase in MM decomposition takes place even if the reaction mixture is allowed to stand for three days.

5.3 Effect of acids and heating on the decomposition of MM

MM is very sensitive to UV-light and decomposes immediately in the presence of UV-light, but on the contrary, it is very stable upon heating. MM does not decompose at all when heated for 2 1/2 hrs. at 80 °C in the presence of 1 to 5 % HCl, 1 to 5 % HNO_3 and 5 % NaCl and even without any addition (Table-6). Even very little MM decomposed when heated at 200 °C in closed quartz vessels (26) under slight overpressure for 1 hour in the presence of 50 % HNO_3 and 40 % HNO_3 + 10 % $HClO_4$ (Table-7). MM only decomposed in the presence of 100 % HNO_3 or 90 % HNO_3 + 10 % $HClO_4$ when heated at 200 °C under slight pressure for 1 hour. However, for the decomposition of MM in water samples it is impossible to add 100 % acids or even 50 % acids because of the low concentration of Hg in water samples. Hence, it is difficult to apply pressure decomposition methods for the analysis of total Hg in water samples containing MM.

Table 6: Decomposition of MM on heating at 80 °C in the presence of acids and NaCl

S.No.	Sample	Hg(ng/ml) measured after 1 (within 1 hour)	2 (heated at 80°C for 2.5 hrs)
1)	1.06 ng/ml Hg as MM + 1.0 % HCl	0.02	0.01
2)	1.06 ng/ml Hg as MM + 5.0 % HCl	0.02	0.04
3)	1.06 ng/ml Hg as MM + 1.0 % HNO_3	0.01	0.01
4)	1.06 ng/ml Hg as MM + 5.0 % HNO_3	0.01	0.01
5)	1.06 ng/ml Hg as MM + 5.0 % NaCl	0.02	0.01
6)	1.06 ng/ml Hg as MM	0.01	0.04

Samples were prepared in pyrex glass flasks covered with Al-foil

Table 7: Decomposition of MM in the presence of acids under pressure at 200 °C

S. No.	Acids added	Hg as MM added (ng/ml)	Digestion time at 200 °C (hrs)	Hg-found ng/ml	% MM decomposed
1.	50 % conc. HNO_3	0.283	1	0.019	6.7
2.	50 % conc. HNO_3	0.283	1	0.00	0.0
3.	100 % conc. HNO_3	0.283	1	0.282	99.6
4.	100 % conc. HNO_3	0.283	1	0.287	101.4
5.	40 % conc. HNO_3 + 10 % conc. $HClO_4$	0.283	1	0.002	0.7
6.	40 % conc. HNO_3 + 10 % conc. $HClO_4$	0.283	1	0.00	0.0
7.	90 % conc. HNO_3 + 10 % conc. $HClO_4$	0.283	1	0.306	108.1
8.	90 % conc. HNO_3 + 10 % conc. $HClO_4$	0.283	1	0.267	94.3

Studies were done for the decomposition of MM in the presence of 50 % HNO_3 and 40 % HNO_3 + 10 % $HClO_4$ and heating at 200 °C under slight overpressure for longer times. It was found that even on heating for 3 hrs. in the presence of 50 % HNO_3 only 25 % MM was decomposed and on heating for 4 hrs. it decreased to 20 %, which may be due to some losses of Hg (fig. 10). It shows that more than 25 % MM is not decomposed in the presence of 50 % HNO_3. When heated for 3 hrs. in the presence of 40 % HNO_3 + 10 % $HClO_4$ only 34 % of MM was decomposed and on heating for 4 hrs it decreased to 29 %, which may be due to some losses of Hg (fig. 10). Therefore, it is difficult to decompose MM more than 34 % in the presence of 40 % HNO_3 + 10 % $HClO_4$.

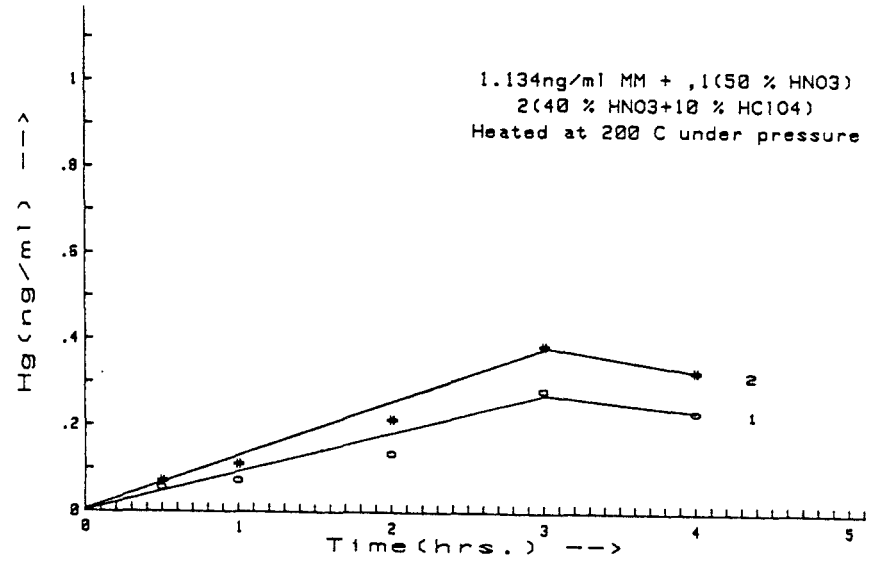

Fig. 10: Decomposition studies of MM in the presence of acids on heating.

5.4 Decomposition of MM in the presence of cystein and different reagents and effect of UV-irradiation

It has been reported that humic substances and sulfhydryl compounds are present in sediments, sea water and other compartments of the environment. Cystein was selected for a case study to see the decomposition and analysis of MM as Hg in aqueous samples in the presence of this compound.

5.4.1 Decomposition of MM in the presence of cystein and different reagents

It can be seen that in the presence of 1 % HCl + 0.05 % cystein and UV-irradiation for 3 hrs only 52 % Hg decomposed to ionic form to be analysed by CVAAS and when allowed to stand for 3 days it decreased to 22 % (Table-8). In the presence of 1 % HNO_3 + 0.05 % cystein and UV irradiation only 45 % Hg was found to be in ionic form and it decreased to 41 % on standing for 3 days. In the presence of 5.0 % NaCl + 0.05 % cystein and UV irradiation only 69 % Hg was in ionic form and decreased to 45 % on standing. Similarly in the presence of 0.05 % cystein only and UV-irradiation 53 % Hg was available and decreased to 47 % on standing for three days.

Table 8: Decomposition of MM and analysis of Hg in the presence of different reagents und cystein

S. No.	Sample	Hg (ng/ml) measured after within 1 hr.	3 hrs. UV	% Hg	3 days	% Hg
1.	1.03 ng/ml MM + 1.0 % HCl	0.06	1.01	98	0.93	90
2.	1.03 ng/ml MM + 1.0 % HNO_3	0.04	0.98	95	0.95	92
3.	1.03 ng/ml MM + 5.0 % NaCl	0.03	1.01	98	1.01	98
4.	1.03 ng/ml MM +	0.03	0.99	96	1.00	97
5.	1.03 ng/ml MM + 1.0 % HCl + 0.05 % cystein	0.04	0.54	52	0.23	22
6.	1.03 ng/ml MM + 1.0 % HNO_3 + 0.05 % cystein	0.05	0.46	45	0.42	41
7.	1.03 ng/ml MM + 5.0 % NaCl + 0.05 % cystein	0.04	0.71	69	0.46	45
8.	1.03 ng/ml MM + + 0.05 % cystein	0.04	0.55	53	0.49	47.6

5.4.2 Decomposition of MM in the presence of cystein alone

MM was exposed to UV-light for different times at two concentrations of cystein i.e., 0.01 % and 0.05 % (fig. 11). At first the amount of ionic Hg available increased and then it decreased when exposed for a longer period to UV. In the whole experiment the detectable mercury was more for 0.01 % cystein and less for 0.05 % cystein, but it was never 100 % and decreased to 64 % for 0.01 % cystein and to 14.6 % for 0.05 % cystein. Thus losses for higher concentrations of cystein are more pronounced.

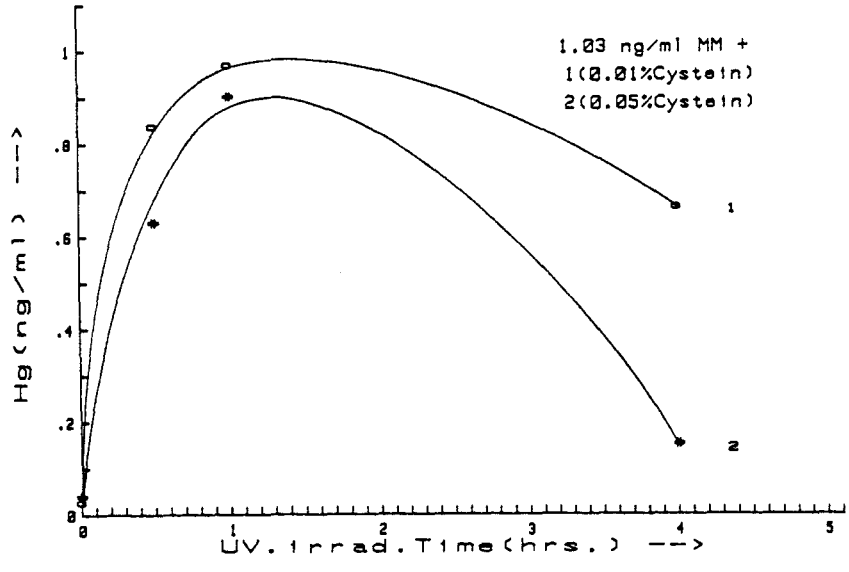

Fig. 11: Decomposition studies of MM in the presence of cystein alone and UV-irradiation

5.4.3 Decomposition of MM in the presence of NaCl + cystein

As sea water and many other environmental samples contain NaCl, it was intended to investigate the decomposition of MM in the presence of 5 % NaCl. In this case also at first the detectable Hg increased and then decreased with longer UV-irradiation. But here the final detectable Hg was in opposite as against to cystein alone. For 0.01 % cystein it decreased to 11.6 % and for 0.05 % cystein it decreased to 22 % (fig.12).

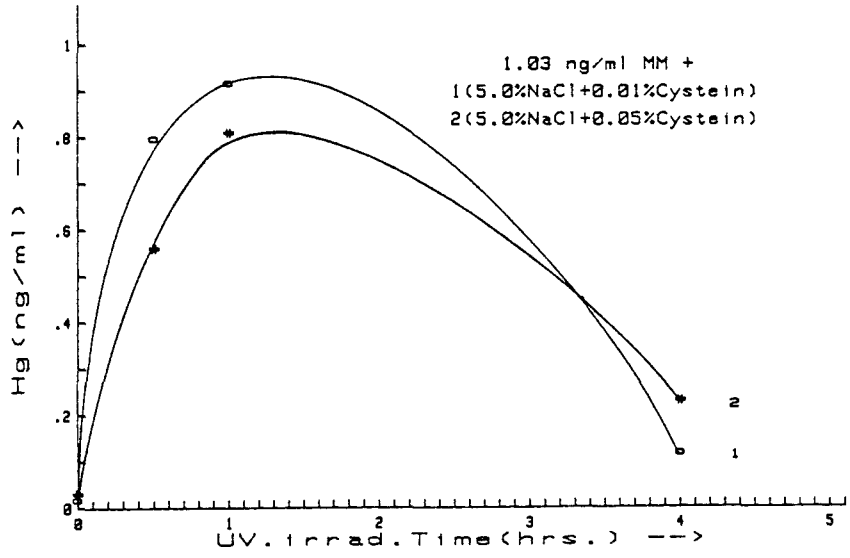

Fig. 12: Decomposition studies of MM in the presence of NaCl, cystein and UV-irradiation.

5.4.4 Decomposition of MM in the presence of cystein and different concentrations of HCl

Decomposition studies of MM were done at different concentrations of HCl and a constant concentration of cystein. The decomposition of MM is studied in the presence of 1 to 10 % HCl and 0.1 % cystein (fig. 13). In the case of 1.0 % HCl, there is an increase in detectable Hg and then it decreases with increase in UV-irradiation time to 42 %. In the case of 10 % HCl, however, there is an increase in detectable Hg with increase in UV-irradiation time and reaches up to 87 % of the total Hg.

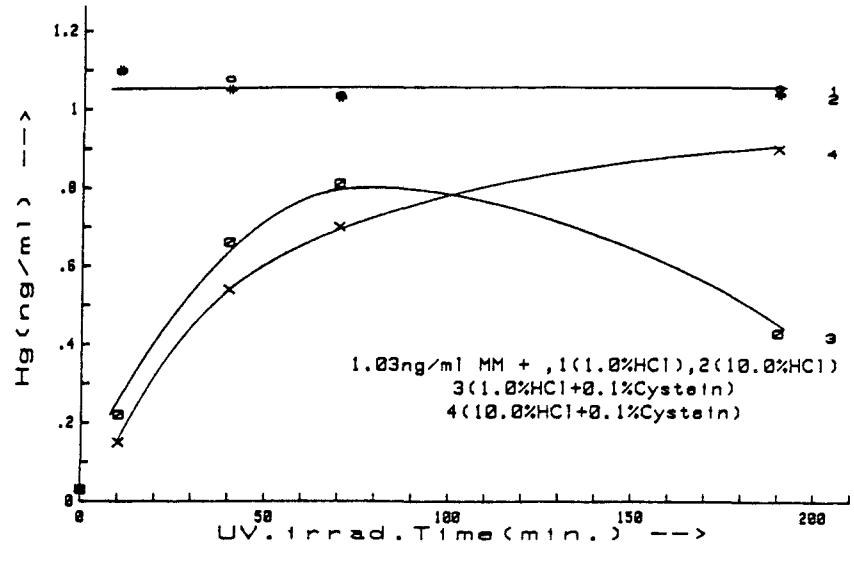

Fig. 13: Decomposition studies of MM in the presence of HCl, HCl + cystein and UV-irradiation.

Detectable Hg in the presence of 0.05 % cystein and different concentrations of HCl is shown in fig. 14 after UV-irradiation. Detectable Hg is at its minimum at 2.0 M HCl which is 61 % of the total Hg and the ratio of cystein to HCl is 0.0025 at the minimum. Towards lower and higher concentrations of HCl the detectable Hg increases.

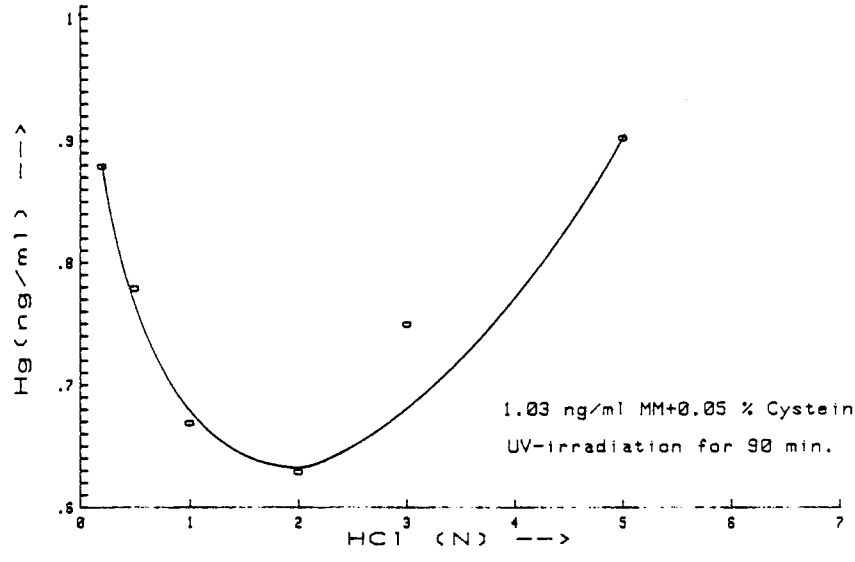

Fig. 14: Decomposition of MM in the presence of different concentrations of HCl, cystein and UV-light.

5.4.5 Decomposition of MM in the presence of HCl and different concentrations of cystein

In the presence of a constant concentraton of HCl and varying concentrations of cystein and after UV-irradiation at first the detectable mercury decreases and then it increases (fig. 15). Detectable mercury is a minimum at 0.2 M HCl and 0.005 % cystein which is 22 % of the total mercury and the ratio of cystein to HCl is 0.0025 at the minimum. Now the ratio of cystein to HCl remains the same (fig. 14, 15) either the concentrations of HCl or that of cystein are changed. Thus the maximum mercury goes into an by CVAAS undetectable form at a ratio of 0.0025 for cystein to HCl, which means that small additions of HCl to water samples which may contain cystein or other sulfhydryl compounds can cause losses for the detectable mercury.

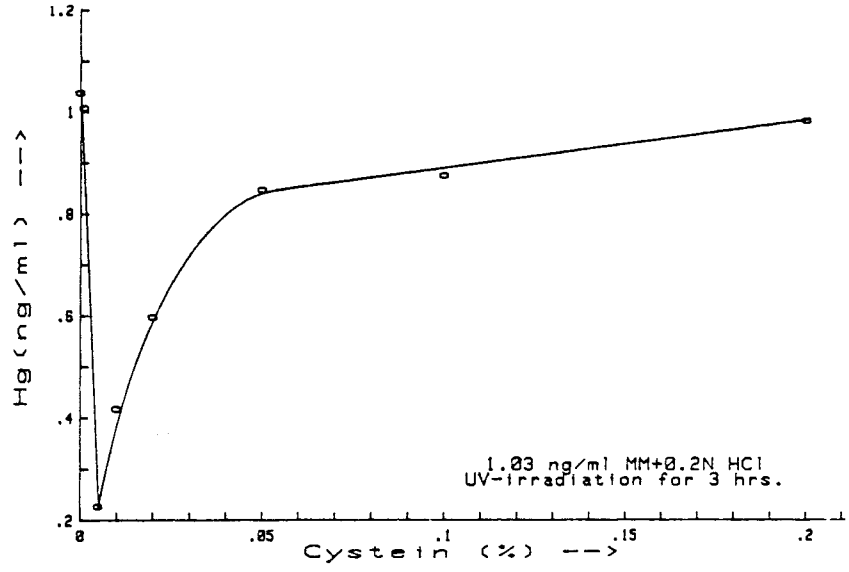

Fig. 15: Decomposition of MM in the presence of HCl and different concentrations of cystein and UV-light.

In fig. 16 is shown that for 0.1 M HCl and different concentrations of cystein the detectable mercury at first increases then decreases with the increase in UV-irradiation time. Finally the detectable mercury by CVAAS for 0.01 % cystein is 37.8 % and for 0.05 % cystein is 68 %.

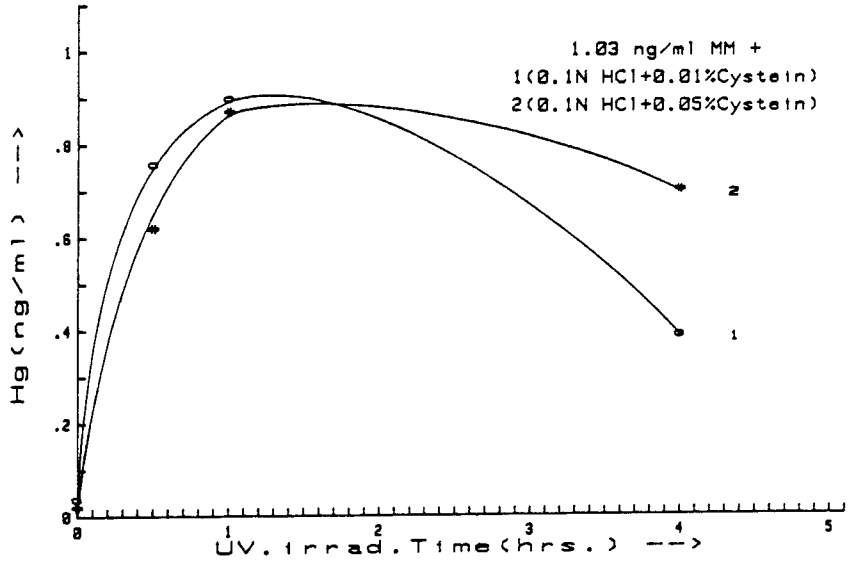

Fig. 16: Decomposition studies of MM in the presence of 0.1 M HCl, different concentrations of cystein and UV-light.

In fig. 17 is shown that for 2.5 M HCl and different concentrations of cystein the detectable mercury increases with the increase in UV-irradiation time.

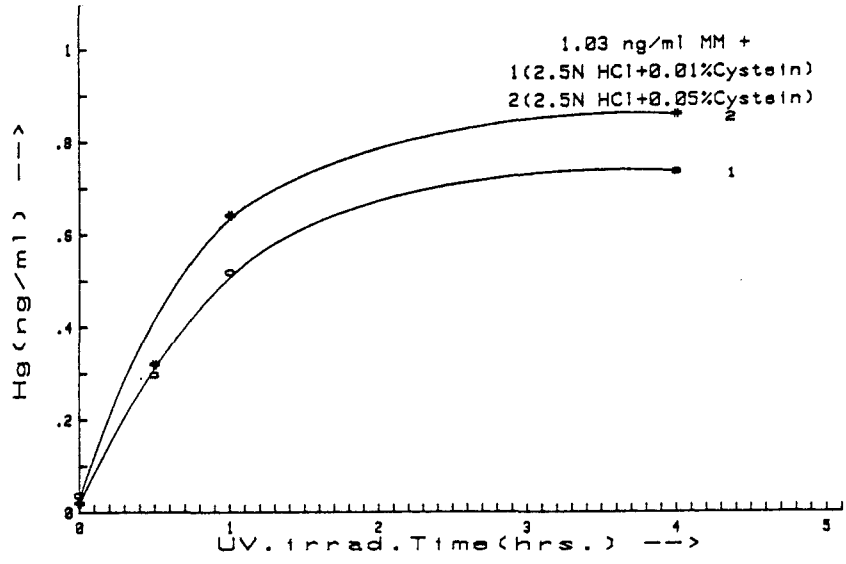

Fig. 17: Decomposition studies of MM in the presence of 2.5 M HCl, different concentrations of cystein and UV-light.

From figs. 11,12,13 and 16 it can be seen that in the presence of cystein, the maximum for detectable mercury is reached after one hour UV-irradiation. With increase in UV-irradiation time, the amount of detectable Hg decreases. As it will be explained later this decrease in Hg is not due to the reformation of MM, but possibly the formation of some sulfide, or other stable mercury compounds.

5.4.6 Decomposition studies of MM in the presence of cystein, NaCl and HCl

In fig. 18 a curve is shown for the decomposition of MM in the presence of cystein, NaCl and increasing concentrations of HCl. From this curve it can be seen that at 0.5 N HCl concentration the detectable Hg is at its minimum. At this minimum the cystein to HCl ratio is 0.008. If the concentration of NaCl is also added to HCl then the ratio of cystein to chloride for this minimum becomes 0.005.

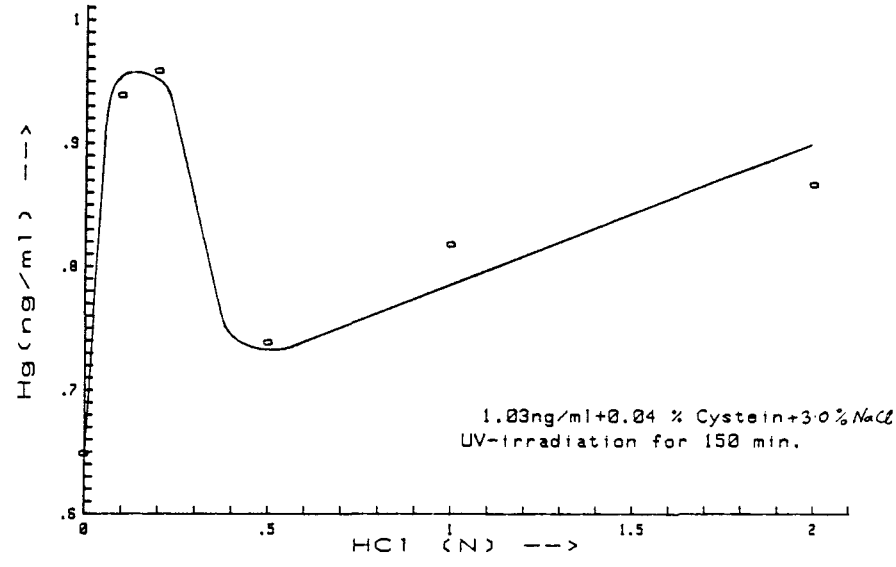

Fig. 18: Decomposition of MM in the presence of cystein + NaCl at different concentrations of HCl and UV-light.

5.4.7 Decomposition of MM in the presence of cystein and NaCl

In fig. 19 is shown the curve for the decomposition of MM in the presence of NaCl and increasing concentrations of cystein. It can be seen that the minimum detectable Hg is at 0.01 % cystein and 4.0 % NaCl and the ratio of cystein to NaCl at the minimum is 0.0025 and this was also the case for HCl (fig. 15).

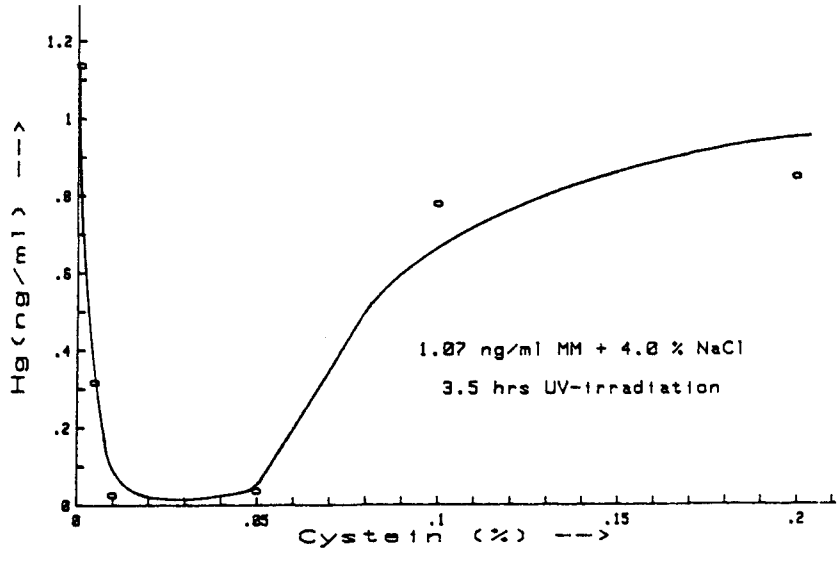

Fig. 19: Decomposition of MM in the presence of 4.0 % NaCl and different concentrations of cystein and UV-light.

But here the ratio is from 0.0025 to 0.0125. Therefore a wide range for losses of MM is obvious. Actually this may be a typical case for sea water which contains 3 - 5 % NaCl and different concentrations of humic substances that may cause losses of MM from sea water which may be the reason why very little or negligible MM is found in water samples as compared to biological materials.

5.4.8 Decomposition of MM in the presence of cystein and different concentrations of HNO_3

In fig. 20 is shown the decomposition of MM in the presence of cystein at different concentrations of HNO_3 and UV-irradiation. At lower concentrations of HNO_3 the detectable MM is less, then it increases. At about 1.4 N HNO_3 it is again at a minimum, then it increases and then decreases. Decrease in decomposition of MM at higher concentrations is mainly due to HNO_3 alone, but the initital decrease may be due to cystein.

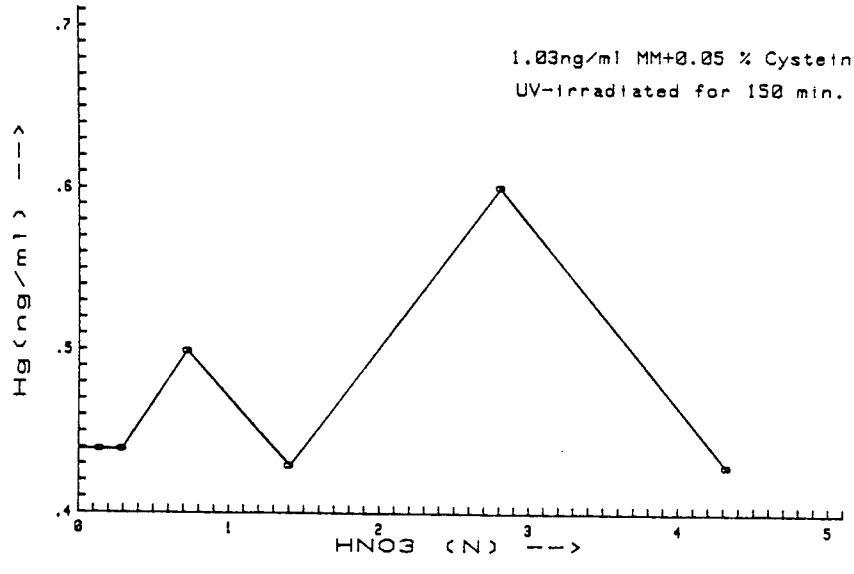

Fig. 20: Decomposition of MM in the presence of cystein at different concentrations of HNO_3 and UV-light.

5.4.9 Decomposition studies of MM in the presence of cystein and other reagents using Hg-203-labelled

To see the disappearance of MM after its decomposition in the presence of cystein and different reagents, experiments were done using labelled MM as ^{203}Hg (Table-9). Samples were UV-irradiated for 2 hrs. then more HCl was added and extracted with toluene. In the presence of 2.0 % HNO_3 + 0.05 % cystein, 30 % of the added MM was not decomposed, in the presence of 5.0 % HNO_3 + 0.05 % cystein, 55 % of the added MM was not decomposed to ionic Hg. In the presence of 5 % NaCl + 0.05 % cystein more than 92 % MM was decomposed to ionic Hg. However, in the presence of 5 % HCl + 0.05 % cystein, 96 % MM was decomposed. In the presence of 0.005 % cystein only, nearly all the MM was decomposed and was in aqueous solution.

Table 9: Decomposition studies of MM with activity measurements of MM labelled with ^{203}Hg

S. No.	Sample	Hg^{203} activity measurement (counts/min) 1	2	Hg(%) 3	4
1.	Hg^{203} MM + 2.0 % HNO_3 + 0.05 % cystein	10022	2756	30.55	69.45
2.	Hg^{203} MM + 5.0 % HNO_3 + 0.05 % cystein	9676	4803	55.11	44.89
3.	Hg^{203} MM + 5.0 % HCl + 0.05 % cystein	10438	344	3.55	96.45
4.	Hg^{203} MM + 5.0 % NaCl + 0.05 % cystein	10333	730	7.89	92.11
6.	Hg^{203} MM + + 0.005% cystein	10998	36	0.37	99.63

1) = Total activity, (samples were UV-irradiated for 2 hrs and then more HCl was added and extracted with Toluene)

2) = Activity in Toluene extract

3) = Hg in Toluene as MM

4) = Hg in Aq. Phase

5.4.10 Decomposition studies of MM in the presence of cystein and other reagents using GLC

In Table 10 the values of MM are given of MM recovered after its decomposition in the presence of cystein and different reagents and UV-irradiation. In the presence of HNO_3 + cystein some MM is recovered and was not decomposed. However, in the presence of HCl + cystein nearly all the MM was decomposed after UV-irradiation.

Table 10: Decomposition studies of MM by Gas-Liquid Chromatography

Sample	MM-added ppm	MM-Recovered ppm	% MM Recovered
MM + 0.5 % conc. HNO_3 + 0.01 % cystein	1.15	0.074	5.83
MM + 1.0 % conc. HNO_3 + 0.01 % cystein	1.15	0.222	17.48
MM + 2.0 % conc. HNO_3 + 0.01 % cystein	1.15	0.141	11.1
MM + 5.0 % conc. HNO_3 + 0.01 % cystein	1.15	0.334	26.30
MM + 0.5 % conc. HCl + 0.01 % cystein	1.15	0.0	0.0
MM + 1.0 % conc. HCl + 0.01 % cystein	1.15	0.0	0.0
MM + 2.0 % conc. HCl + 0.01 % cystein	1.15	0.0	0.0
MM + 5.0 % conc. HCl + 0.01 % cystein	1.15	0.0	0.0
standard	1.15	1.27	100

20 ml of each of the samples 1 to 8 was exposed to UV-light for 2.5 hrs., than 5.0 ml of conc. HCl was added to each and extracted with 20 ml of Toluene and MM was analysed by GLC

5.5 Stability studies of MM in the presence of different reagents and different containers

5.5.1 Storage of ionic mercury

Experiments were performed to see the losses during storage of mercury in pyrex glass flasks in the presence of 0.1 M HCl, 0.1 M NaOH, 0.1 M HNO_3, 5.0 % NaCl and without addition of anything (fig. 21) . It can be seen that the rate of losses

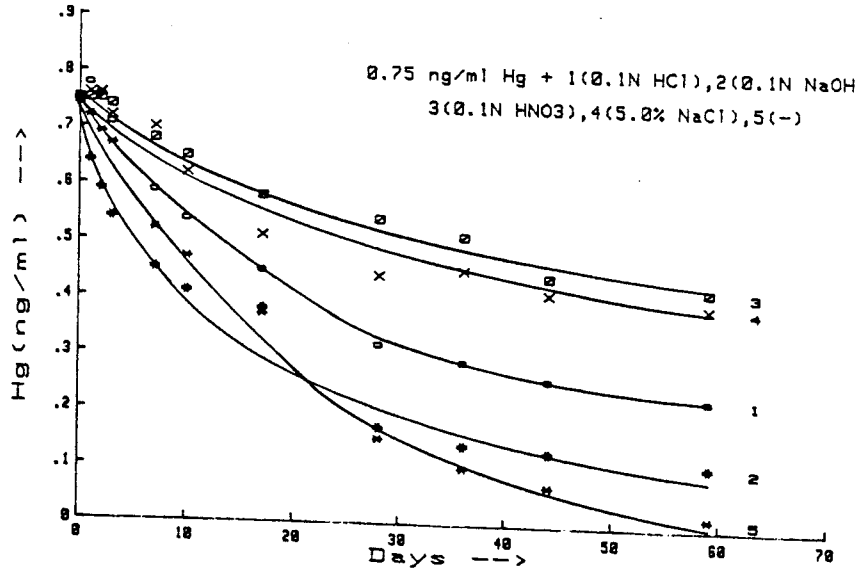

Fig. 21: Long-term storage studies of ionic Hg in the presence of HCl, HNO_3, NaCl and NaOH

of Hg is minimum for HNO_3 followed by NaCl, HCl, NaOH and without any addition. Thus best preservatives for ionic Hg for normal use are HNO_3 > NaCl > HCl > NaOH. Now to understand a little bit about the losses of Hg from these solutions, the empty flasks were washed with HNO_3 to recover any adsorbed Hg on the walls of the flasks (Table-11). It can be seen from Table-11 that in case of 0.1 M HCl after a storage of 136 days only 6.67 % Hg was in dissolved form, 11.6 % was adsorbed on the walls of the flasks and 81.7 % Hg disappeared. In the case of 0.1 M NaOH, 2.67 % Hg was in solution, 7.01 % was adsorbed on the walls of the flask and 90.3 % Hg disappeared. For 0.1 M HNO_3, 50.67 % Hg remained in solution, 4.62 % was adsorbed on the walls of the flasks and 44.71 % Hg disappeared. For 5.0 % NaCl 45.33 % Hg was in solution, 11.71 % was adsorbed on the walls of the flask and 42.95 % disappeared. In case of de-ionized water only 1.33 % was in solution, 14.95 % was adsorbed on the walls of the flask and 83.72 % disappeared.

Table 11: Stability and losses of ionic Hg after storage period of 4.5 months

Sample	Reagents Added	Total Hg/ 250 ml Added	Hg in solution After 4.5 months	Hg Recovered from the Walls of the flask after 4.5 months	Tot. Hg after 4.5 months	Hg-Disappear
		ng	ng	ng	ng	%
A	0.1 N HCl	187.5	12.50 6.67 %	21.82 11.6 %	34.32	153.18 (81.7 %)
B	0.1 N NaOH	187.5	5.0 2.67 %	13.15 7.01 %	18.15	169.35 (90.3 %)
C	0.1 N HNO_3	187.5	95.0 50.67 %	8.67 4.62 %	103.67	83.83 (44.71 %)
D	5.0 % NaCl	187.5	85.0 45.33 %	21.96 11.71 %	106.96	80.54 (42.95 %)
E		187.5	2.5 1.33 %	28.03 14.95 %	30.53	156.97 (83.72 %)

Due to these results the from storage point of view best reagents are: HNO_3 > NaCl > HCl > NaOH > H_2O only in the given order. HNO_3 is the best and H_2O only is the worst.

From the point of view of mercury disappearance, mercury disappeared from these solutions in the order: NaOH > H_2O only > HCl > HNO_3 > NaCl. The maximum mercury disappeared from NaOH solution and minimum from NaCl solution.

From the point of view of mercury adsorption on the walls of the flasks the order is: H_2O only > NaCl > HCl > NaOH > HNO_3. Maximum mercury was adsorbed on the walls of the flask without any addition, in the presence of chloride also enough mercury was adsorbed on the walls of the flask. Adsorption of mercury was minimum on the walls of the flask in the presence of HNO_3.

5.5.2 Stability studies of MM in pyrex glass flasks covered with Al-foil

Stability studies of MM in pyrex glass flasks in the presence of different reagents were done for more than 60 days. In the presence of water only (fig. 22) MM decomposed very rapidly. More than 75 % MM decomposed within 10 days. Losses of total mercury were also significant but less than the rate of decomposition of MM. Ionic mercury at first increased and then decreased.

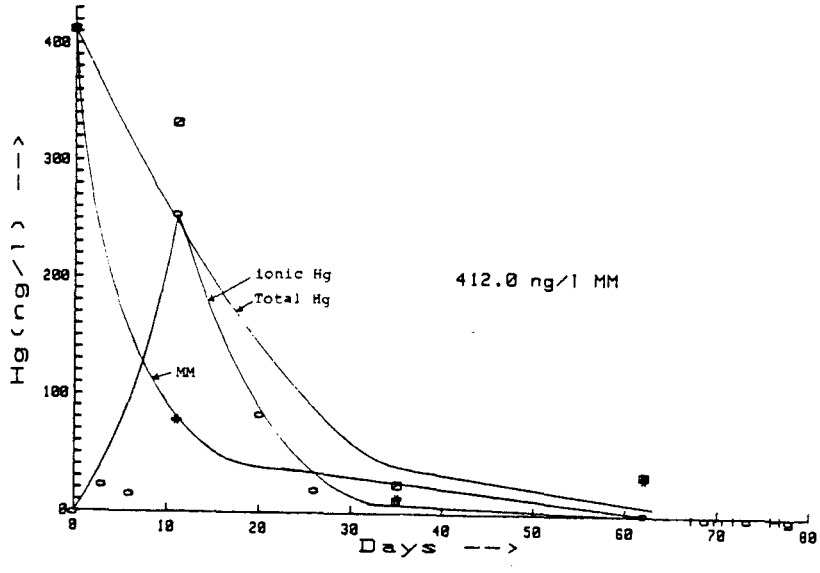

Fig. 22: Stability studies of MM in pyrex glass flasks covered with Al-foil.

Decomposition of MM in the presence of 1.0 % HCl was much less (fig. 23). The amount of MM decomposed was available as ionic mercury. There were some losses in total mercury.

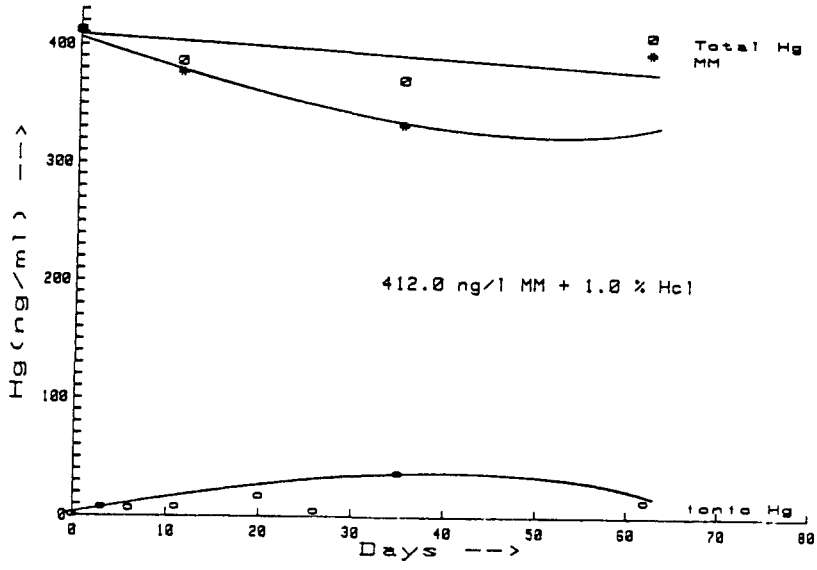

Fig. 23: Stability studies of MM in pyrex glass flasks covered with Al-foil.

In fig. 24 is shown the stability of MM in the presence of 10 % HCl. After two month's storage 10 % MM decomposed and was available as ionic mercury. But the amount of total mercury remained constant during the storage period.

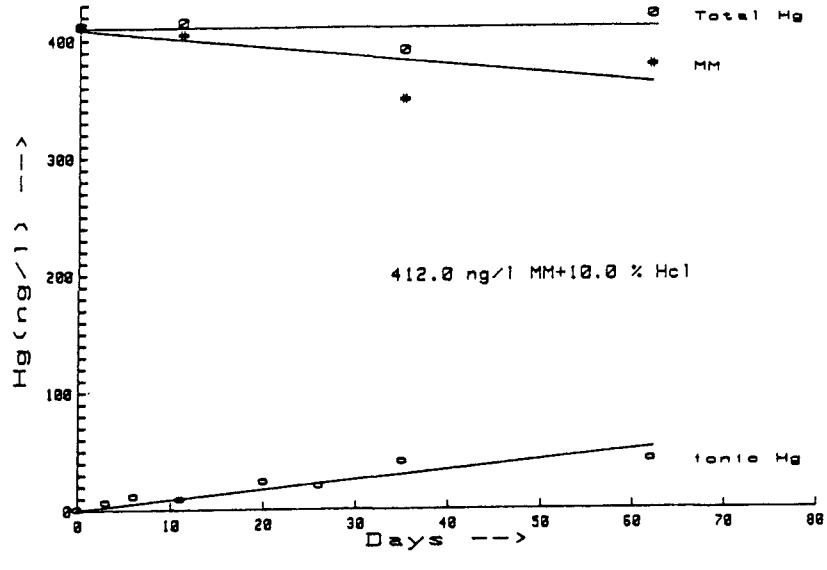

Fig. 24: Stability studies of MM in pyrex glass flasks covered with Al-foil.

In the presence of 1.0 % HNO_3, MM was relatively much stable (fig. 25).

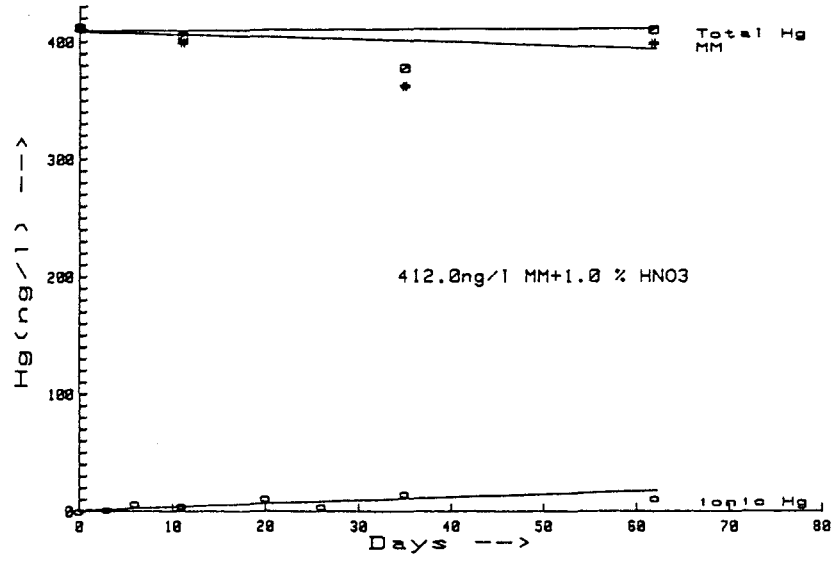

Fig. 25: Stability studies of MM in pyrex glass flasks covered with Al-foil.

With 1.0 % H_2SO_4 MM also did not decompose (fig. 26) so quickly. After a storage period of 2 months 87.3 % of MM was available, total mercury Hg was 91.0 % and as ionic mercury 3.7 % was measured.

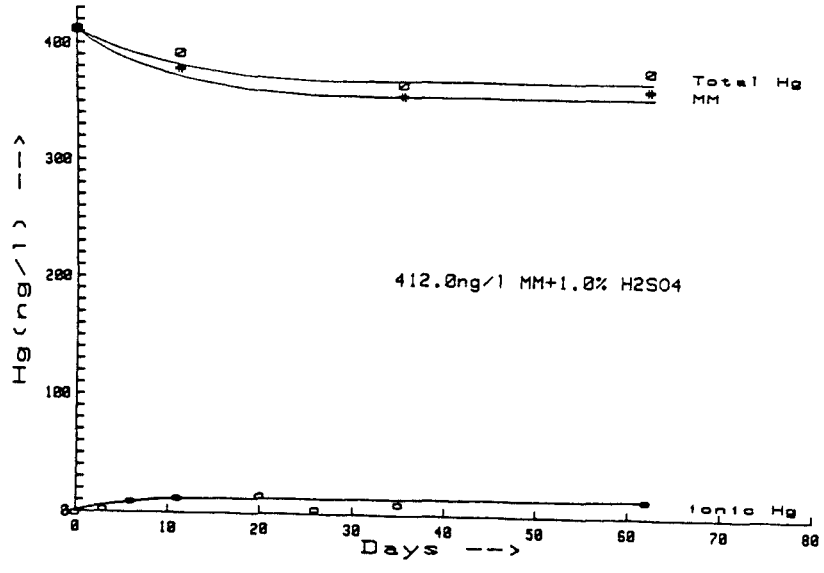

Fig. 26: Stability studies of MM in pyrex glass flasks covered with Al-foil.

In the presence of 3.0 % NaCl, the stability of MM (fig. 27) was like that of HCl with the only difference that ionic mercury produced with decomposition of MM disappeared more rapidly than the rate of decomposition of MM on long-term standing.

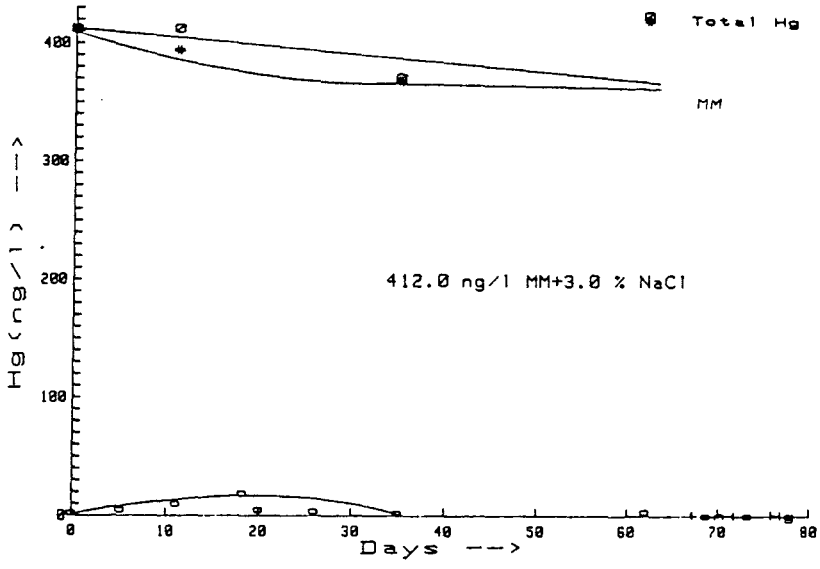

Fig. 27: Stability studies of MM in pyrex glass flasks covered with Al-foil.

From these studies it can be concluded that MM decomposes very rapidly in the presence of water only but is quite stable in the presence of some acids or NaCl.

5.5.3 Stability studies of MM in polyethylene bottles (250 ml) uncovered and covered without and with HCl

MM decomposes very rapidly when no reagents are added (fig. 28). The only difference from glass flasks is that here ionic mercury produced disappears more rapidly than in glass flasks. It also shows that the stability of MM in glass and polyethylene is nearly the same but losses of ionic mercury take place much more rapidly from polyethylene bottles. The latter is due to reduction of ionic to metallic mercury on the surface and diffusion of mercury through the walls (27).

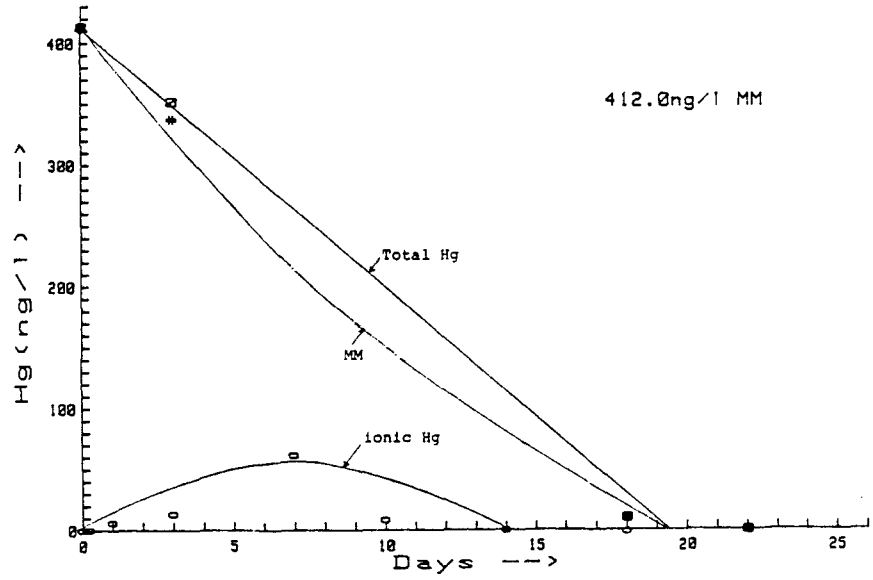

Fig. 28: Stability studies of MM in polyethylene bottles (250 ml) uncovered.

In the presence of 1.0 % HCl more than 91 % MM was present after a storage period of 22 days. But the ionic mercury produced dis-appeared more, therefore, there was decrease in total mercury (fig. 29).

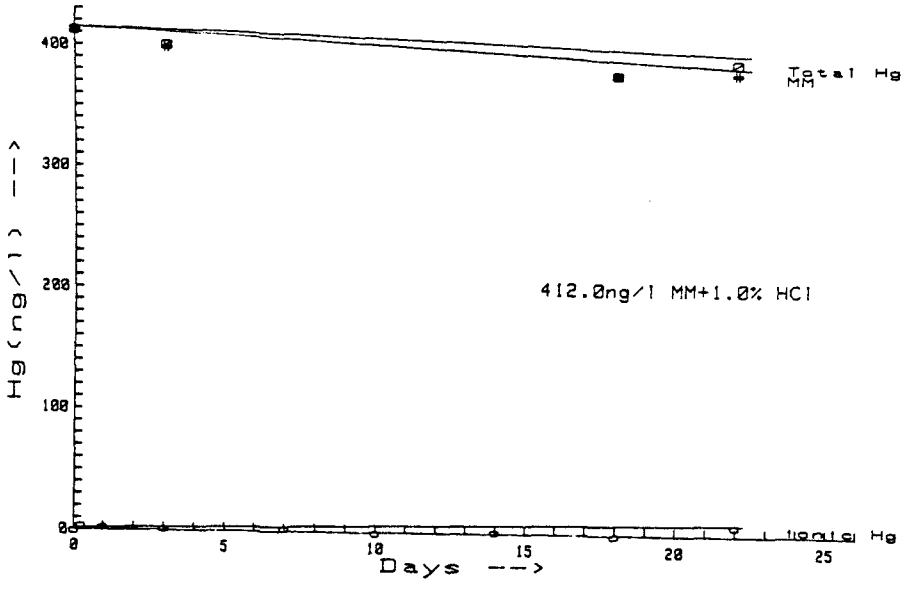

Fig. 29: Stability studies of MM in polyethylene bottles (250 ml), uncovered.

For 10 % HCl the decomposition of MM was more rapid than for 1 % HCl (fig. 30). After a storage period of 22 days about 84 % MM was present. But the ionic mercury produced here did not disappear, therefore, the amount of total mercury nearly remained the same. In figs. 28-30, the polyethylene bottles were kept uncovered. The same experiments were repeated with polyethylene bottles covered with Al-foil (figs. 31-33) to see if there was any influence of light. As it can be seen from (figs. 31-33) no influence of light was observed. The reason may be that very little UV-light can pass through polyethylene bottles.

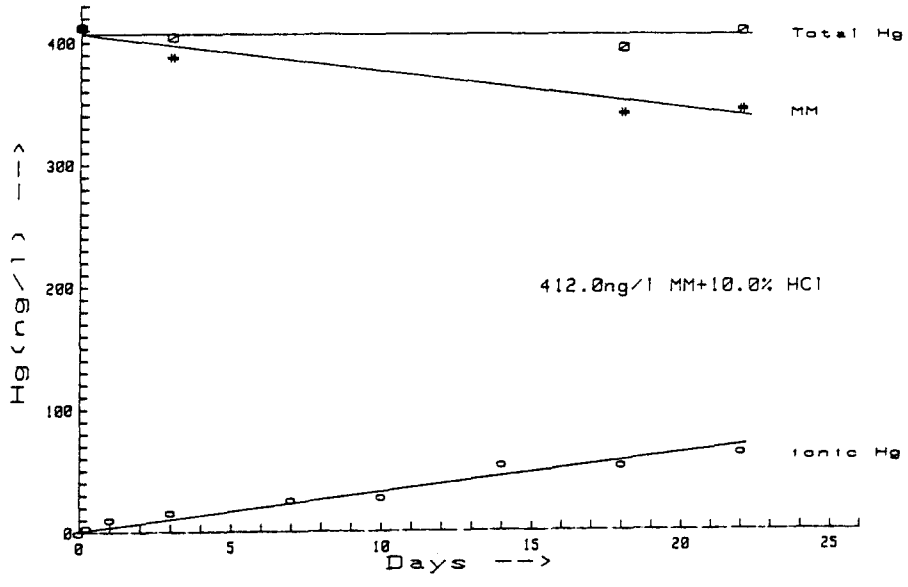

Fig. 30: Stability studies of MM in polyethylene bottles (250 ml), uncovered.

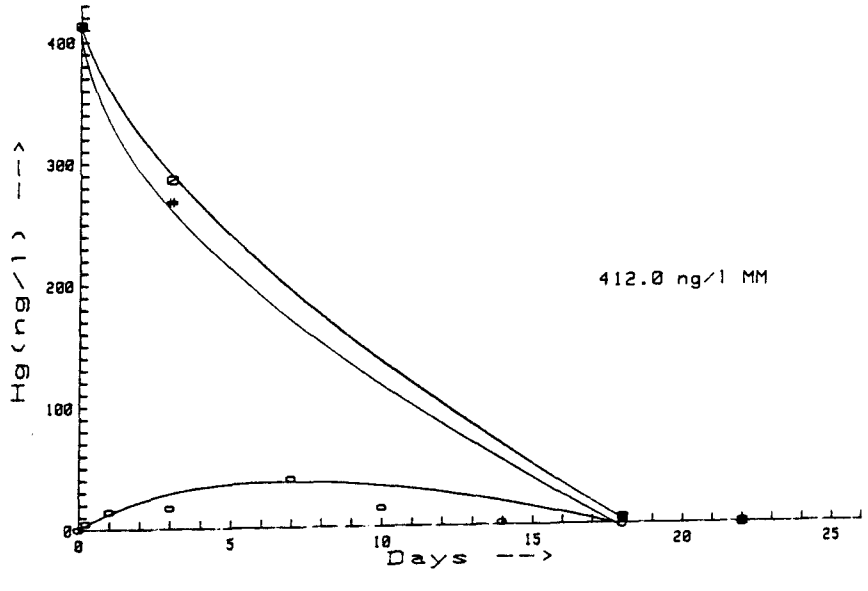

Fig. 31: Stability studies of MM in polyethylene bottles (250 ml), covered with Al-foil.

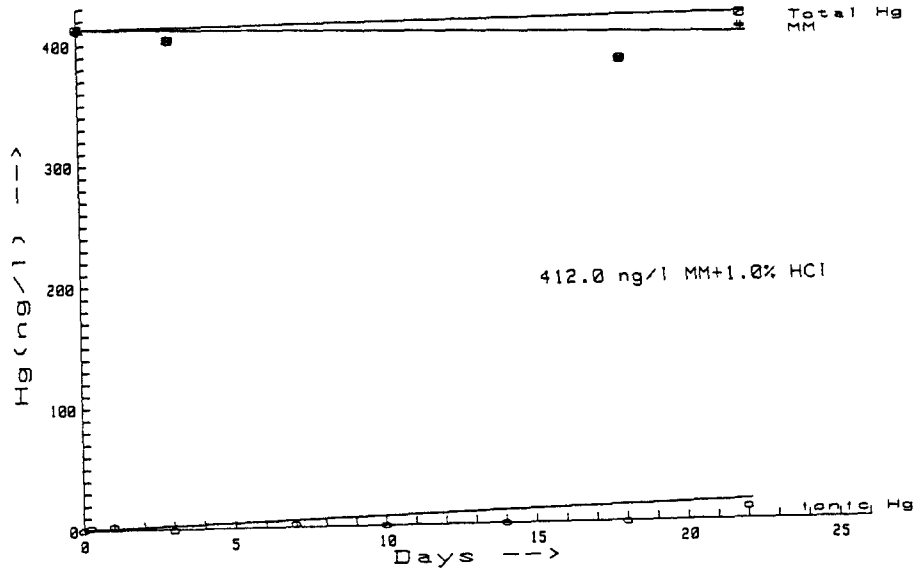

Fig. 32: Stability studies of MM in polyethylene bottles (250 ml), covered with Al-foil.

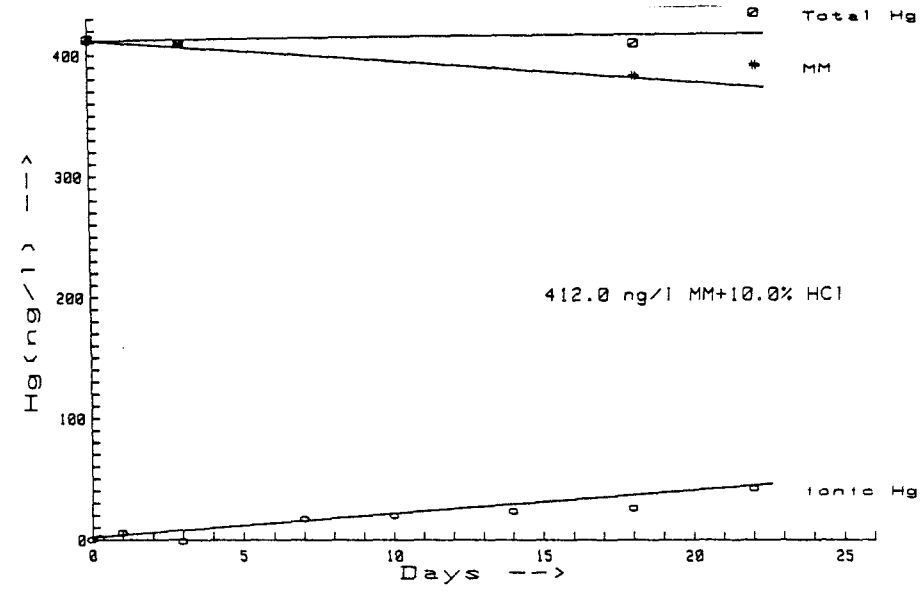

Fig. 33: Stability of MM in polyethylene bottles (250 ml), covered with Al-foil.

5.5.4 Stability studies of MM in polyethylene bottles (500 ml) uncovered

Previous experiments about the stability of MM in polyethylene bottles were done using higher concentrations of MM (27). Normally for water sampling purposes polyethylene bottles ranging from 1 l to 20 l are used, particularly for sea water and river water sampling etc. It was thought to be appropriate to see the stability of MM at low levels in polyethylene bottles kept as such uncovered in the laboratory.

Without any addition, the decomposition of MM (fig. 34) appears be similar to that at higher concentration of MM (fig. 28), but here the rate of decomposition appeared to be somewhat faster. However the disappearance of ionic mercury remains faster as in the earlier case.

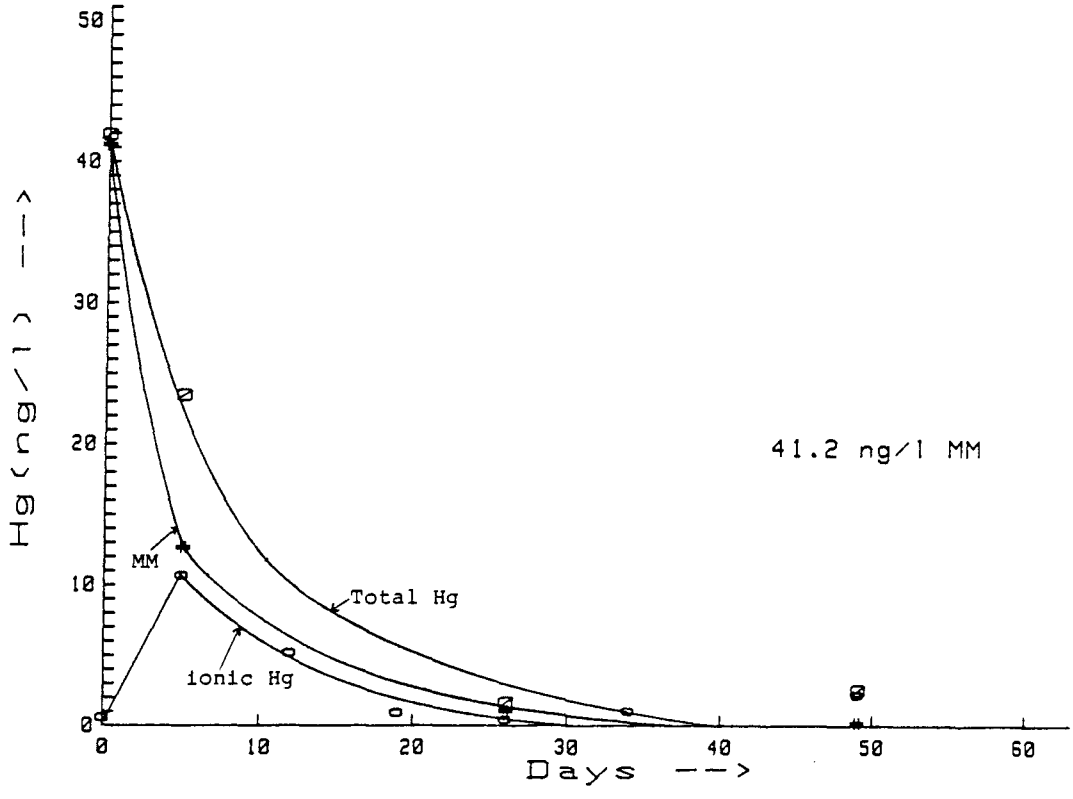

Fig. 34: Stability of MM in polyethylene bottles (500 ml), kept as such in the Lab.

In the presence of 1.0 % NaCl (fig. 35) the decomposition of MM is nearly similar to that without any addition (fig. 34). In the presence of 5.0 % NaCl MM is more stabilized (fig. 36). After a storage period of 50 days 86.6 % MM was present. The rate of disappearance of ionic mercury was faster than the rate of decomposition of MM.

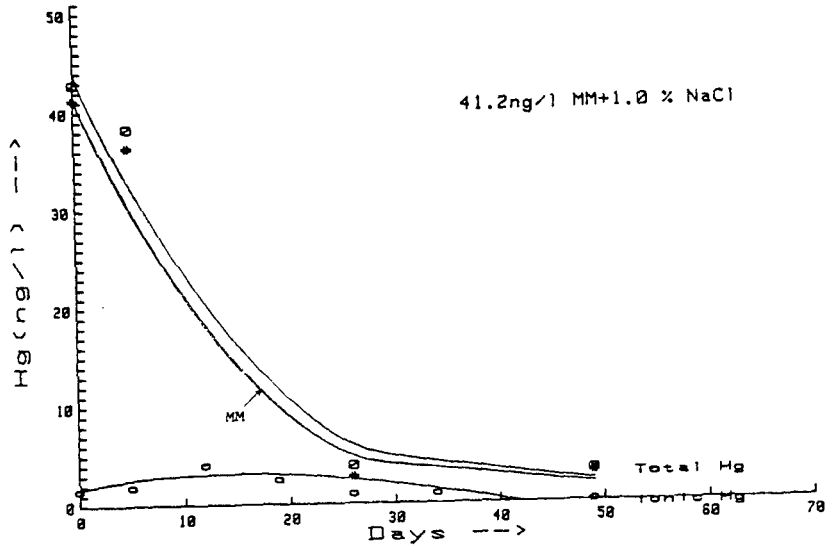

Fig. 35: Stability of MM in polyethylene bottles (500 ml), kept as such in the Lab.

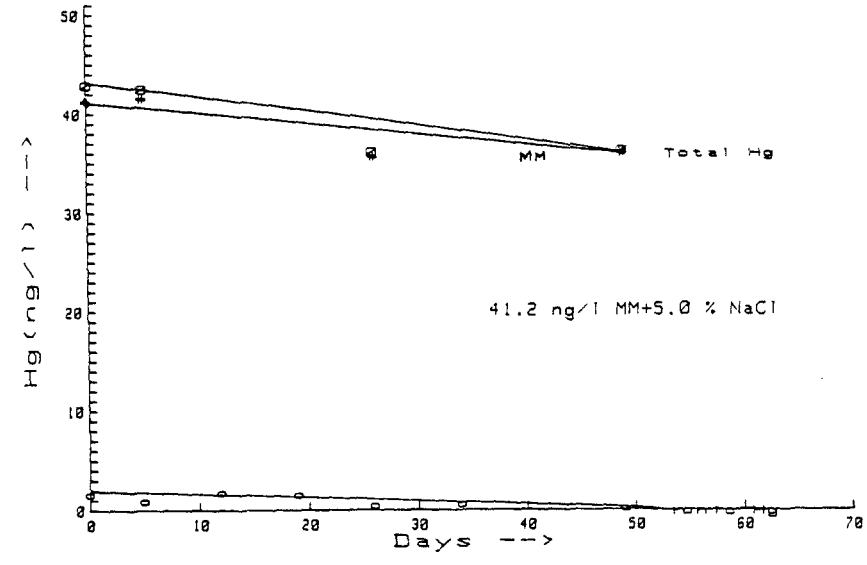

Fig. 36: Stability of MM in polyethylene bottles (500 ml), kept as such in the Lab.

The behaviour of MM in the presence of 1.0 % HCl was entirely different (fig. 37) from that at higher concentrations of MM in small polyethylene bottles (fig-29). Here MM decomposed much rapidly, but there were very little losses of ionic mercury. Thus the amount of MM decreased and the amount of ionic mercury increased and total mercury remained nearly constant. Within 5 days nearly 50 % of MM decomposed and after 25 days nearly all MM was decomposed.

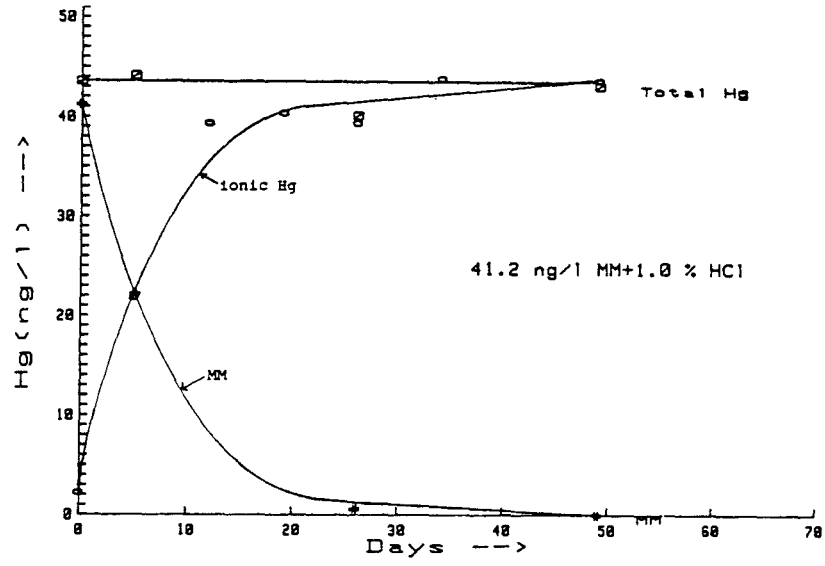

Fig. 37: Stability of MM in polyethylene bottles (500 ml), kept as such in the Lab.

In the presence of 1.0 % HNO_3 MM does not decompose so quickly, after a storage period of 49 days more than 65 % MM was still present. The rate of disappearance of ionic mercury from the solution was also much less as compared to in the presence of H_2O only, HCl and NaCl. Here the rate of disappearance of ionic mercury is nearly equal to the rate of decomposition of MM (fig. 38).

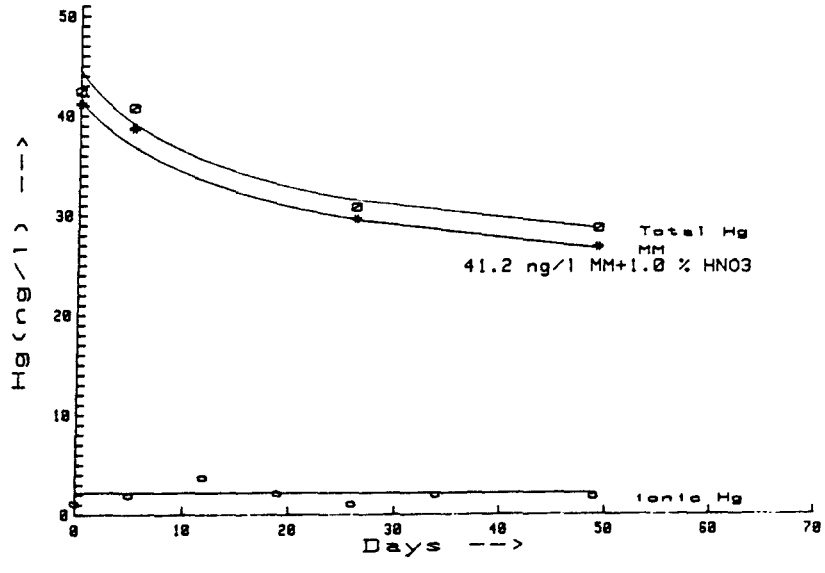

Fig. 38: Stability of MM in polyethylene bottles (500 ml), kept as such in the Lab.

5.5.5 Stability studies of MM in clear PTFE bottles (1 l) kept uncovered

PTFE bottles are also frequently used for sampling and storage purposes. It appeared appropriate to do stability studies of MM in these bottles at low concentrations of MM.

In the presence of water only the decomposition profile of MM (fig. 39) looked similar to that in polyethylene bottles (fig. 34), but here the rate of loss of ionic mercury produced is relatively low compared to polyethylene bottles and looks even better than in pyrex glass (fig-24) flaks.

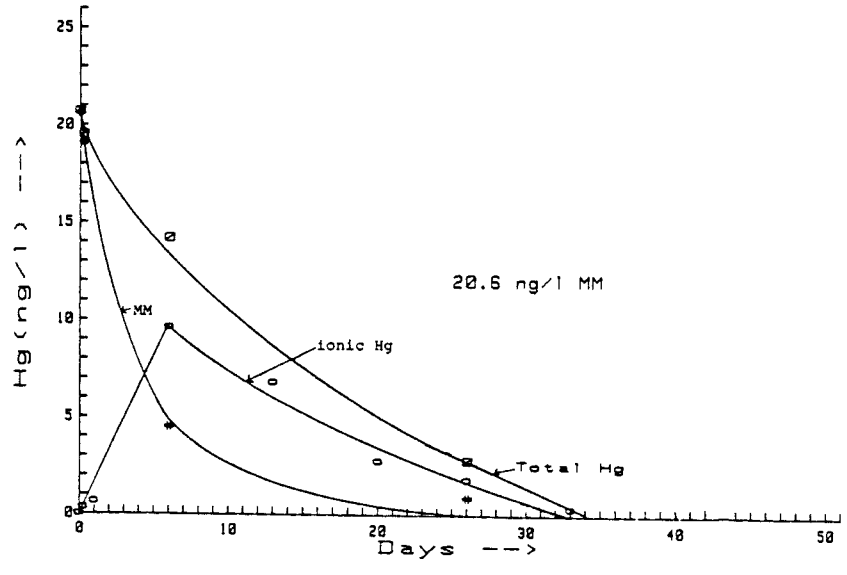

Fig. 39: Decomposition studies of MM in PTFE bottles (clear) kept as such in the Lab.

For 5.0 % NaCl (fig. 40), MM is well stabilized and more than 82 % MM was present after a storage period of 26 days. Here the behaviour is similar to that in polyethylene (fig. 36) and in pyrex glass flasks (fig. 27), which shows that 5.0 % NaCl has its own stabilizing effect irrespective of the container material.

For 1.0 % HCl MM is well stabilized (fig. 41) and after 26 days more than 83 % MM was available. Here the behaviour is like that in pyrex glass flasks (fig-25).

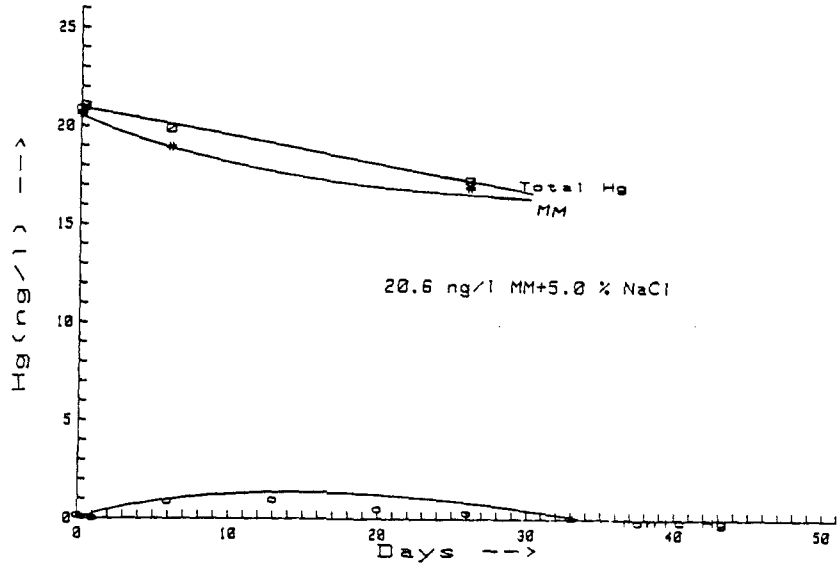

Fig. 40: Decomposition of MM in PTFE bottles (clear), kept as such in the Lab.

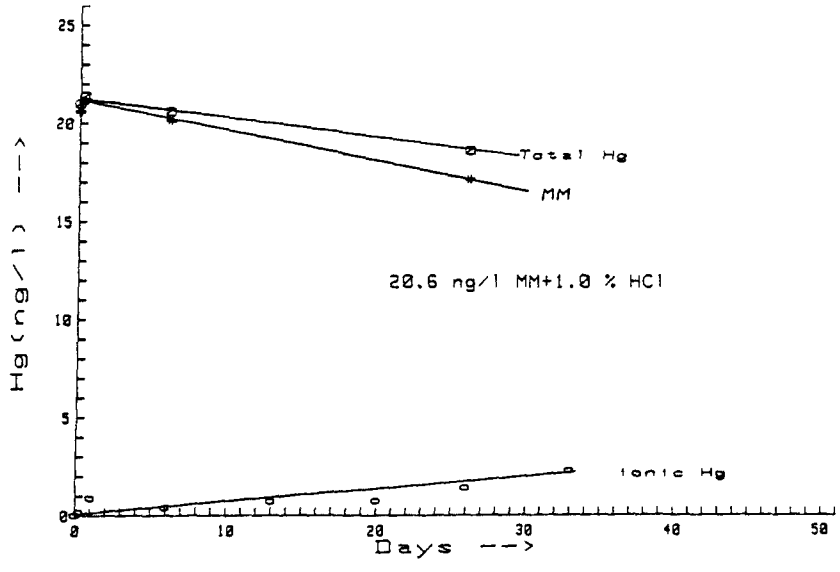

Fig. 41: Decomposition of MM in PTFE bottles (clear), kept as such in the Lab.

When 5.0 % HCl is added, the rate of decomposition of MM increases (fig. 42) and consequently the amount of ionic mercury increases as well, but the total mercury remains nearly constant. Nearly a similar behavior was observed for polyethylene bottles in the presence of 1.0 % HCl (fig. 37). For PTFE bottles 1.0 % HCl has remarkably stabilized MM.

It was observed, however, for small polyethylene bottles (figs. 29,30) that decomposition of MM increased with an increase in HCl concentration, although to a lesser extent

than here. Similar is the trend for pyrex glass flasks (figs. 23,24) but the rate of decomposition remains very small. This shows that higher concentrations of HCl increase decomposition of MM with different rates in different types of materials and this decomposition rate increases significantly under the influence of light.

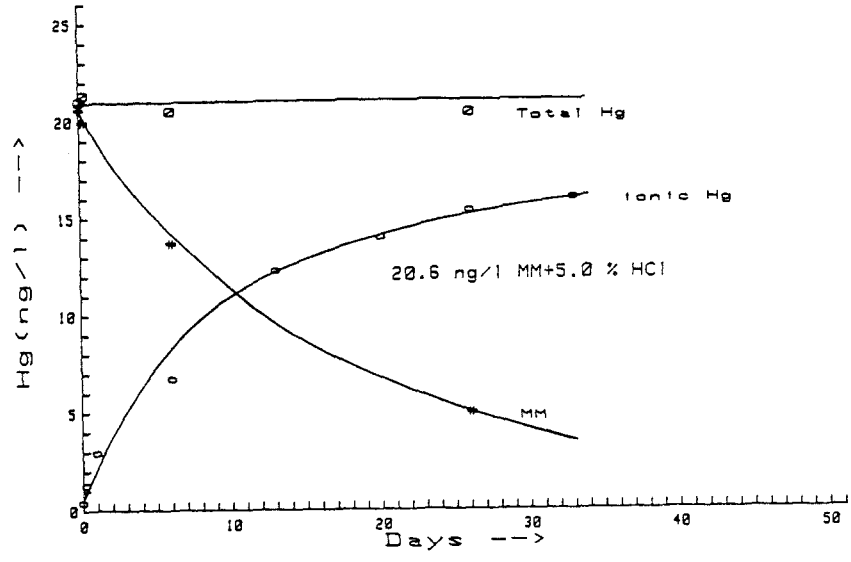

Fig. 42: Decomposition of MM in PTFE bottles (clear), kept such in the Lab.

Addition of 1.0 % HNO_3 also stabilized MM (fig-43). After a storage period of 26 days more than 68 % MM was still present. The Stabilization effect of 1.0 % HNO_3 in polyethylne bottles (fig. 38) and glass flasks (fig. 25) is nearly the same but with different rates of decomposition for MM.

In the presence of 5.0 % HNO_3 (fig. 44) at first MM decreased, then increased and again decreased. This is quite clear. The first decrease in MM is because it is difficult to decompose MM with UV-light in the presence of higher concentrations of HNO_3, but on storage for a few days periods, more MM could be decomposed, but on long term storage, the MM decomposed more, thus decreasing its concentration in the solution.

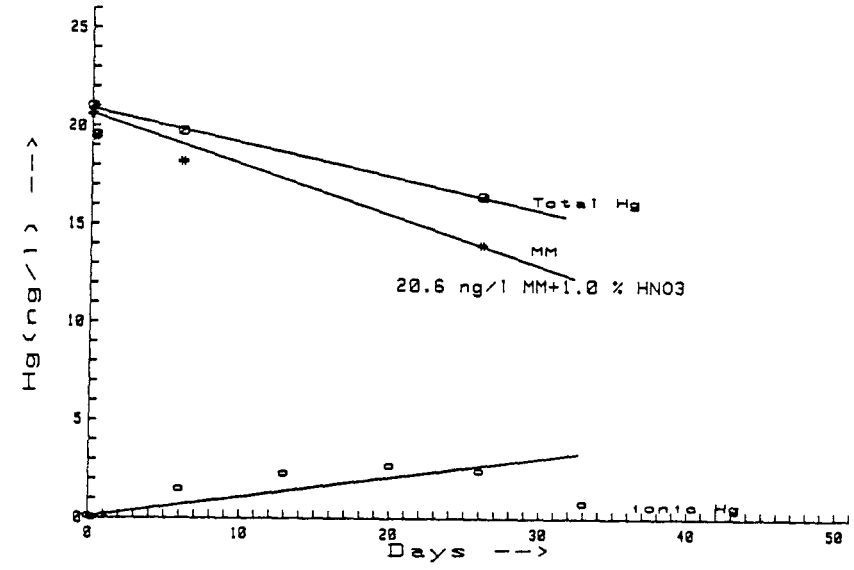

Fig. 43: Decomposition of MM in PTFE bottles (clear), kept as such in the Lab.

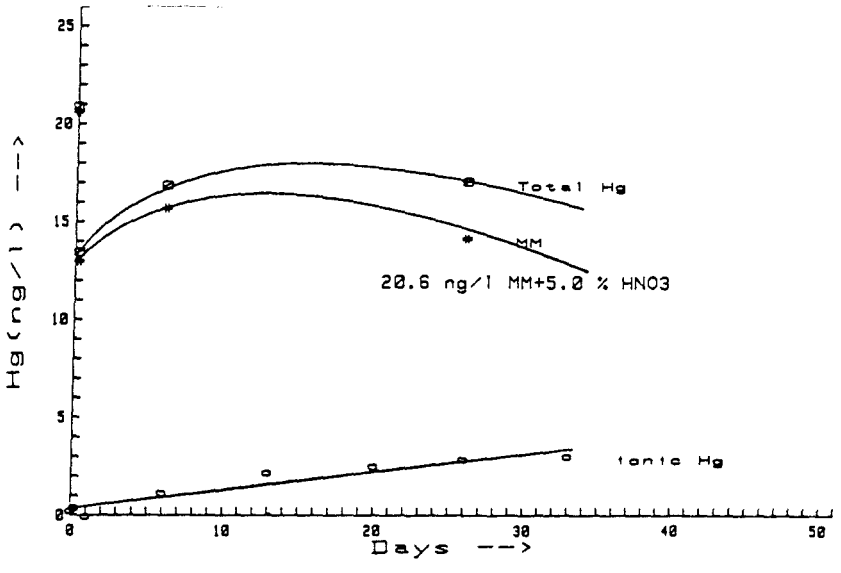

Fig. 44: Decomposition of MM in PTFE bottles kept as such in the Lab.

6. CONCLUSIONS

No MM was decomposed in the reduction step with 10 % $SnCl_2$ + 20 % H_2SO_4 for subsequent analysis by AAS.

When NaCl and HCl both are added together at the concentrations commonly used for extraction of MM, they cause also decomposition of MM. Nearly 40 % of MM decomposes under these conditions within one day in pyrex glass flasks covered with Al-foil. 100 % MM decomposes within 4 hours in quartz glass flasks kept as such in the laboratory.

In the presence of chlorides UV-light decomposes MM very quickly.

In the presence of alkali (NaOH) MM is not decomposed so quickly with UV-light. The rate of decomposition decreases with decreasing NaOH concentration.

Nearly all the acids investigated and different combinations of acids up to 25 % do not decompose MM even when allowed to stand for $\sim$ 3 days.

1 to 20 % HNO_3 in the presence of 3 % NaCl does not decompose MM over a period of 40 days.

Decomposition of MM with UV-light decreases with increasing HNO_3 concentration and becomes difficult when the HNO_3 concentration is more than 25 %.

Acids in the presence of H_2O_2 decompose MM in the order $HNO_3 > H_2SO_4 = HClO_4 > HCl$. Keeping H_2O_2 concentration constant and increasing acid concentrations does not increase decomposition of MM. With increasing H_2O_2 concentration, decomposition of MM increases. Decomposition of MM takes place after the addition of acids + H_2O_2 and does not increase if reaction time is prolonged.

MM is not decomposed on heating at 80 ^{o}C for 2 1/2 hrs in the presence of 5 % acids. In the presence of 50 % HNO_3, 40 % HNO_3 + 10 % $HClO_4$, heated at 200 ^{o}C under slight overpressure for 1 hr less than 10 % MM is decomposed. In the presence of 100 % acids and heating at 200 ^{o}C for 1 hr complete decomposition of MM takes place. In the presence of 50 % acids when heated at 200 ^{o}C, the decomposition of MM increases with increasing heating time, but maximum decomposition is 25 % for 50 % HNO_3 and 34 % is for 40 % HNO_3 + 10 % $HClO_4$.

It is very difficult to decompose MM in the presence of cystein and becomes even difficult when cystein to chloride concentration ratios are low, which is mainly the case in environmental samples.

Storage of MM with cystein and exposure to UV-light for longer times decreases the amount of decomposed ionic Hg to be analysed by CVAAS.

Our experiments have shown that in the presence of cystein and other reagents, MM is decomposed nearly completely by UV-irradiation, but most of the decomposed mercury from MM was not detectable by CVAAS, which suggests formation of some sulfides or other complexes which are not reduced by $SnCl_2$ + H_2SO_4 to elemental mercury.

Stability and losses of mercury were studied in the presence of some common reagents. For total losses of mercury, the order is H_2O only $>$ NaOH $>$ HCl $>$ NaCl $>$ HNO_3. For disappearance of mercury, the order is NaOH $>$ H_2O only $>$ HCl $>$ HNO_3 $>$ NaCl. For adsorption of mercury on the walls, the order is H_2O only $>$ NaCl $>$ HCl $>$ NaOH $>$ HNO_3.

In pyrex glass flasks, MM decomposes rapidly in the presence of H_2O only and was stabilized reasonably in the presence of 1 % HCl, 10 % HCl, 1.0 % HNO_3, 1.0 % H_2SO_4 and 3.0 % NaCl.

In polyethylene bottles (250 ml), MM decomposes very rapidly in the presence of H_2O only, but was stabilized reasonably in the presence of 1.0 % HCl and 10.0 % HCl. No appreciable effect was observed when bottles were kept covered or as such in the laboratory.

In polyethylene bottles (500 ml) at lower concentrations of MM, MM decomposes very rapidly in the presence of H_2O only. MM also decomposes very rapidly in the presence of 1.0 % NaCl and 1.0 % HCl. However, 5.0 % NaCl and 1.0 % HNO_3 stabilized MM reasonably.

In PTFE (clear) bottles at lower concentrations of MM, MM decomposes rapidly in the presence of H_2O only. MM also decomposed in the presence of 5.0 % HCl. But MM was stabilized reasonably in the presence of 1.0 % HCl, 5.0 % NaCl, 1.0 % HNO_3 and 5.0 % HNO_3

From these findings we recommended as preservatives for MM 3.0 to 5.0 % NaCl followed by 1.0 % HNO_3 and 1.0 to 5.0 % HCl. The containers should be protected from light which is of particular importance for HCl.

7. ACKNOWLEDGEMENT

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